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SEPARATION OF SATURATES AND AROMATICS FROM SYNCRUDE MIDDLE DISTILLATE

FINAL REPORT

by

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EXECUTIVE SUMMARY

In order to attain self-sufficiency in transportation fuels, Canada must develop new technologies to upgrade heavy oils and tar sands. At present, a high degree of hydrogenation is required to produce diesel and jet fuels from synthetic middle distillates, and some valuable components are lost (hydrocracked to light petroleum gases and naphtha).

Separation of the aromatics from the saturated hydrocarbons of synthetic middle distillates would result in a smaller stream that requires severe hydrogenation, and the saturates stream would have a high cetane number and low smoke point - ideal for various transportation fuel formulations. Solvent extraction is a promising way of effecting the saturates-aromatics separation.

The present research project has generated extraction data on two different synthetic middle distillates, representing the two major Canadian sources of synthetic crude (Suncor and Syncrude tar sand upgrading plants). Liquid-liquid equilibrium data were obtained on systems of the middle distillates with 12 different organic solvents, and sulphur dioxide as the "base case". The solvents could then be rated on properties such as distribution coefficients for saturates and aromatics, and the two most promising organic solvents were selected for further study.

More comprehensive phase behaviour measurements were conducted with acetonitrile, dimethylformamide and sulphur dioxide as the solvents, at three different temperatures and several solvent/oil ratios for each. This allowed the construction of phase diagrams and (graphical) calculation of the number of theoretical plates required to achieve the desired degree of separation between saturates and aromatics. In this phase of the studies, it was also possible to establish that subgroups of the aromatic and saturated hydrocarbons have different distribution characteristics from the main groups; e.g., alkylbenzenes are preferentially extracted over condensed aromatics.

Subsequent investigations concentrated on acetonitrile as the solvent, which (at the time) seemed to offer the best chances for commercial success. Twenty-three "survey" counter-current extractions of Syncrude and Suncor middle distillates with acetonitrile

were conducted in a continuous pilot plant extractor, to establish the optimum process conditions. The equipment was also used in a solvent recycle mode, to approximate commercial conditions more closely. Appreciable quantities of raffinate and extract were produced in the pilot plant experiments, and were examined with regards to product quality.

A solvent extraction process to separate the aromatic and saturated hydrocarbon components of synthetic middle distillates seems technically feasible. Specification diesel and jet fuels can be produced by this means. Among the organic solvents studied, acetonitrile has been the most promising. It appears to form double non-consolute pseudo-ternary systems with middle distillate saturates and aromatics; this suggests that extracts of high "purity" (95 wt% aromatics content or more) can be readily obtained with acetonitrile, at room temperature. Raffinate quality is also very satisfactory. However, when acetonitrile is distilled off from the extract, some of the hydrocarbons contaminate the distillate. This difficulty must be overcome before acetonitrile extraction can become a viable process. Meanwhile, sulphur dioxide (Edeleanu process) remains the leading contender to effect the desired separations.

Literature data on the sulphur dioxide extraction of middle distillates should be reviewed in conjunction with the present project's results, to estimate the economics of employing this solvent at low temperature. If the economics of SO_2 extraction seem favourable, a pilot plant should be constructed, to generate further technical and economic data on the process. The feasibility of acetonitrile extraction of synthetic middle distillates should also be further investigated. Improved separation of acetonitrile from the raffinate may be possible just by adding a small amount of water prior to fractionation.

A worthwhile research project would be to employ fractions of synthetic middle distillates obtained by organic solvent extraction for elucidating the relationships between fuel quality and composition. It has been found, for instance, that subgroup selectivity effects, such as preferential extraction of alkylbenzenes compared to benzocycloparaffins, often improve diesel fuel quality by two Cetane numbers or more.

1. INTRODUCTION

1.1 Objectives

The overall objective of this project was to evaluate the feasibility of producing high-quality transportation fuels from synthetic crude middle distillate fractions by solvent extraction. This processing will produce saturate and aromatic-rich streams from low-quality middle distillates, derived from synthetic crudes available commercially in Canadian refineries. The saturate stream will readily make high-quality transportation fuels, while the aromatic-rich stream will be available for severe hydrogenation without degradation of the high-quality components.

The specific objectives of this project were:

1) comparison of the behaviour of candidate extraction solvents with that of sulphur dioxide (SO_2),

2) selection of a promising solvent, and design, construction and operation of a bench-scale extraction unit with synthetic crude middle distillates,

3) evaluation of the economic feasibility of an optimum solvent extraction process for the production of high-quality transportation fuels.

1.2 Justification

In order to attain energy self sufficiency in transportation fuels, Canada must develop new and innovative technologies to produce them. This is due to the dilemma of having an expanding market in diesel and Jet fuels, while having a resource base largely of heavy oils and tar sands, which yield low-quality middle distillates, unsuitable for the manufacturing of these fuels. Syncrude middle distillate can be converted to diesel and Jet fuels, but a high degree of hydrogenation is required. Even so, the hydrogenated products still barely meet the minimum quality specifications for such fuels. Furthermore, hydrogenation of the whole middle distillate stream is somewhat counterproductive, in that high quality components are cracked to light petroleum gases and naphtha.

Separation of aromatic and saturate components in the middle distillate would be useful from both a product and processing point of view. Segregation of saturates, particularly paraffins, would provide a stream with a high cetane number and low smoke point, which would be ideal for diesel and Jet fuels. The aromatic stream coproduced would have very low fuel quality; however, it would be approximately half the size of the original middle distillate stream and contain components less likely to crack. As a result, severe hydrogenation of this stream would require smaller units, produce less light ends and generally be more economical.

Aromatic and saturate components cannot be separated by distillation since they have the same boiling range. Chemical separation would be too expensive, but solvent extraction - which relies on the differences in solvation properties between species to effect a separation - is potentially useful. The petroleum industry has often employed and still uses solvent extraction as a unit operation for accomplishing aromatics separations. Sulphur dioxide (Edeleanu process) was originally used to extract aromatics from kerosene, to make it smokeless (1). Glycols and other oxygenates are employed in the Udex and Sulfolane processes to extract benzene, toluene and xylenes from reformate and pyrolysis gasoline. Furfural, N-methyl pyrrolidone and phenol are used to extract high boiling aromatics from lube oil basestocks.

Solvent extraction would appear to be capable of separating Syncrude middle distillates into saturate and aromatic streams. The former stream would make a high-quality fuel, while the latter could be upgraded at reduced cost. The combination of the aliphatic stream with the upgraded aromatic stream should result in a greater volumetric yield of quality middle distillate fuels.

1.3 Commercial Experience and Published Research Results on Aromatics Extraction from Middle Distillates

Aromatics extraction from middle distillates is not as common as from lighter and heavier petroleum fractions; nevertheless it has received a fair amount of attention in connection with improving the combustion properties of jet fuels, increasing the cetane number of diesel fuels, and also to provide feedstocks for petrochemicals and carbon black manufacture.

During the 1930's and 40's, some commercial experience was gained in the United States on the extraction of middle distillates with "conventional" solvents: furfural and sulphur dioxide (2). Although these processes were employed primarily to treat cracked stocks (light cycle oil), they appeared to be applicable to straight-run streams as well. (The latter resemble more closely the "synthetic" middle distillates that are dealt with in the present project.) However, the furfural and SO_2 processes did not achieve widespread use in upgrading middle distillates (except for kerosene), and since the 1960's much attention has been paid to novel solvents, showing promise in this area.

Table 1.1 lists the individual solvents that have been considered to extract aromatics from middle distillates - either to improve fuel quality or to obtain petrochemicals. At times, more complex schemes have been developed than "straightforward" solvent extraction; for example, in the REDEX process (3) xylene is exchanged into light cycle oil while the heavy aromatics are extracted into the solvent phase. However, compared to conventional, single-column extraction, REDEX is principally a means to save on utilities; such refinements need not be investigated during the exploratory stage of extraction studies.

One would conclude from the literature survey that there is an excellent chance to develop a solvent extraction process to separate saturates and aromatics from synthetic crude middle distillate fractions, and that several solvents deserve serious consideration.

2. EXPERIMENTAL

2.1 Feedstocks

Two synthetic middle distillate feedstocks were selected for the experimental program. They represented the Syncrude and Suncor tar sand upgrading plants - the only major sources of snythetic crude in Canada.

Syncrude raw middle distillate, a product of the Syncrude fluid coking and hydrotreating process, is fractionated at Petro-Canada's Edmonton Refinery, resulting in a distillate of approximately 160°C to 315°C boiling range. Suncor middle distillate is derived from Suncor "A" stream synthetic crude, a product of the Suncor delayed coking and hydrotreating plant. The latter synthetic crude was fractionated at the Petro-Canada Products Research and Development Centre, to yield a middle distillate of 175°C to 305°C boiling range.

Although many of the physical characteristics of Syncrude and Suncor middle distillates are similar, the chemical compositions are different. Syncrude middle distillate has an aromatics content of approximately 40 wt.% and a Cetane Number of 31, whereas the aromatics content of Suncor middle distillate is only 31 wt.%, with a correspondingly higher Cetane Number of 37. Both feeds were considered good candidates for an extraction process that would increase the Cetane Number to 40 or higher.

Table 2.1 shows the most important physical and chemical properties of typical Syncrude and Suncor middle distillates, and detailed mass spectrometric analyses of two samples are given in Table 2.2.

2.2 Solvents

Almost all the solvents studied in this project had been evaluated in some fashion by other workers (cf. Table 1.1) for the extraction of middle distillates. One or two, like nitroethane, were known to have an affinity to aromatic hydrocarbons, and seemed promising. Table 2.3 lists the solvents that were finally selected for the extraction studies. A few solvents that were also considered but turned out to be miscible with the middle distillates, have been excluded from this table.

Temperature of extraction has a very great effect on the solubility characteristics of solvents. By varying the extraction temperature, the same solvent may show greater changes in solvent characteristics than different solvents compared at the same temperature level (25). In the present

work, the extraction tests were restricted to the temperature range 0-80°C. It was felt that temperatures outside this range would be unattractive to refineries because of the relatively high heating or cooling costs. Whenever possible, extractions were performed at 20, 40 and 60°C. Higher or lower temperatures were dictated by miscibility considerations, and in one case (sulfolane) by the high melting point of the solvent. The final temperatures selected for each solvent are shown in Table 2.3 The basic properties of most of these solvents have been listed in Table 1.1, but are repeated in Table 3.1 for the sake of completeness.

2.3 Analytical Techniques

The minimum amount of analytical information required on raffinate and extract samples was: total aromatics content and residual solvent content. (The saturates content could then be calculated by difference.)

The following four Hydrocarbon Group Type analytical methods were evaluated for use in this project, using a variety of middle distillates.

1. Liquid chromatography - SARA (S = Saturates, A = Aromatics, R = Resins, A = Asphaltenes) (26).

2. Liquid Chromatography (LC) - Method suggested by Sawatzky (27).

3. High Pressure Liquid Chromatography (HPLC).

4. Low Resolution Mass Spectroscopy (LRMS).

Low-resolution mass spectrometry (28) was found to be the best method for the determination of hydrocarbon classes and distributions. Liquid Chromatography (LC) and high performance liquid chromatography (HPLC) were inappropriate, due to the losses of light ends during sample handling and analyses. The residual solvent content of raffinates was determined by gas chromatography.

One advantage of mass spectrometry is that - in addition to giving the overall aromatics and saturates contents of samples - it provides quite detailed information on the types of saturates and aromatics present. Certainly, in an extraction process there could be differences between the selectivities for different subgroups of hydrocarbons, e.g. alkylbenzenes and multi-ring aromatics. Furthermore, this could have a significant influence on product quality.

Table 2.2 shows the amount of detail mass spectrometry has provided - primarily for feeds and raffinates. In the analysis of the extraction data, certain groups of compounds were always pooled, resulting in the following classes of hydrocarbons:

Paraffins
Non-Condensed Cycloparaffins
Condensed Dicycloparaffins
Condensed Polycycloparaffins
Alkylbenzenes
Benzocycloparaffins and Benzodicycloparaffins
Naphthalenes
Balance, including heterocyclic compounds

Usually, even more pooling was performed, so that most of the time this report discusses solvent extraction in terms of saturates-aromatics-solvent pseudo-ternary systems.

2.4 Extraction Techniques and Apparatus

2.4.1 Batch Extraction with Organic Solvents

The extraction apparatus was a jacketed, baffled, 1-litre glass vessel, equipped with stirrer and condenser, as shown in Figure 2.1. The procedure described below was common for all twelve organic solvents studied.

Equal volumes of middle distillate sample and test solvent were weighed and charged to the extraction vessel. The vessel's contents were stirred and allowed to reach the predetermined experimental equilibrium temperature. The mixing continued at the experimental temperature for a minimum of 5 minutes and was then terminated, allowing the phases to disengage for a minimum

of 5 minutes. The resulting raffinate and extract were separated and transferred to sample bottles, through the stopcock located at the bottom of the apparatus. A mass balance was determined for each experiment and samples of the extract and raffinate phases were analyzed.

2.4.2 Sulphur Dioxide Extractions

The extraction of middle distillates with sulphur dioxide was accomplished with an autoclave extraction apparatus, similar to the glass apparatus employed to develop phase equilibrium data. In the procedure, a weighed sample of middle distillate was charged to the 1-litre autoclave shown in Figure 2.2. The vessel was sealed and pressure-tested to 800 kPa with N_2. It was then chilled to -30°C with a dry ice/acetone bath and evacuated to approximately 50 mmHg pressure. The sulphur dioxide was bled into the autoclave, using a beam balance to monitor its weight.

The internal cell mixer and mantle heater were turned on until the experimental temperature was attained. The heater was then turned off and an external bath was used to maintain the necessary temperature. Once the equilibrium temperature had been reached, the middle distillate and solvent were mixed for a minimum of five minutes, followed by phase disengagement for a minimum five minutes. The autoclave was pressurized to 400 kPa with N_2 and aliquot samples of the lower and upper phases were taken in stainless steel bombs (and weighed). The sulphur dioxide was evaporated at 100°C in a fumehood, the hydrocarbon fractions were analyzed and mass balances were calculated.

2.4.3 Batch Simulation of Continuous Counter-Current Extraction

A batch simulation of a three-stage continuous counter-current extraction of Syncrude middle distillate with acetonitrile was carried out. Details of the procedure are described in Treybal (29).

2.4.4 Pilot Plant Extraction

Preliminary work was carried out on a four-foot-long, two-inch diameter glass column, filled with 0.24 inch "Pro-Pak" stainless steel packing. The experiments in this glass column provided information on flooding velocities, phase separation aspects, and in general, were a useful starting point towards designing the required pilot plant.

The next step was estimating the height equivalent of a theoretical plate (H.E.T.P.) in an one-inch diameter stainless steel column - a choice dictated by hardware availability and fabrication considerations. Extractions carried out in a four-foot-long column of this type, with Syncrude middle distillate feed and acetonitrile solvent, at room temperature and a solvent/oil ratio of 1.8 mL/mL, gave the number of transfer units as 1.75, indicating a H.E.T.P. of approximately 2.3 feet. (The packing in this column was 0.16 inch "Pro-Pak" stainless steel.)

The single-stage extraction results suggested that 4 or 5 theoretical plates would be required to reach the desired raffinate and extract qualities: maximum 20% aromatics in the raffinate hydrocarbons, 95% aromatics in the extract. Allowing for reduced efficiency, it was therefore decided to construct a 16-foot long column for the survey and production run (otherwise similar to the 4 ft. x 1" column). The flow rates that were appropriate/practical for this "final" extraction apparatus were: 180-300 mL/h feed and 300-600 mL/h solvent. The unit is described in detail in the Pilot Plant Extraction Unit Operating Manual, which is attached to this report (Appendix I).

Twenty-three survey extraction runs were done on the unit at two temperatures, two feed rates and three solvent-to-oil ratios, to investigate process conditions. The extraction plant was then operated in a solvent recycle mode (production run), in which the solvent was distilled from the raffinate and extract product phases and was continuously recycled as the solvent feed for extraction.

The production run was of approximately 200 hours duration, but only the first 100 hours were conducted in the solvent recycle mode, because the accumulation of light hydrocarbons in the distilled solvent adversely affected raffinate quality. Once this had been discovered, recycling of the solvent was stopped and only fresh solvent was fed to the extraction apparatus. Altogether, 25 litres of raffinate and 8 litres of extract were prepared for large-volume tests.

Following compositional analysis of the "production run" extract and raffinate streams, and diesel-type product analysis of the raffinate, a sample of the raffinate was fractionated (using a 2-litre, 25-plate spinning band distillation apparatus) to a cut point of 300°C. The IBP to 300°C fraction was evaluated as a Jet A product.

3. OVERVIEW OF THE STUDIES

As discussed in Section 2.1, this project has generated extraction data on two different synthetic middle distillates, representing the two major Canadian sources of synthetic crude (Suncor and Syncrude tar sand upgrading plants).

Liquid-liquid equilibrium data were obtained on systems of the middle distillates with 12 different organic solvents, and sulphur dioxide as the "base case" (Table 3.1). The solvents could then be rated on properties such as distribution coefficients for saturates and aromatics, solvent power (see Section 4.2), and the two most promising organic solvents were selected for further study.

More comprehensive phase behaviour measurements were then conducted with acetonitrile, dimethylformamide and sulphur dioxide as the solvents, at three different temperatures and several solvent/oil ratios for each. This allowed the construction of phase diagrams and (graphical) calculation of the number of theoretical plates required to achieve the desired degree of separation between saturates and aromatics. In this phase of

the studies, it was also possible to establish that subgroups of the aromatic and saturated hydrocarbons have different distribution characteristics from the main groups; e.g., alkylbenzenes are preferentially extracted over condensed aromatics. Subsequently it was decided that - all things considered - acetonitrile offered the best chances for commercial success.

The next step was to generate operating data for acetonitrile extraction of Syncrude and Suncor middle distillates, by performing continuous counter-current extractions in a pilot plant unit. Twenty-three "survey runs" were conducted to establish the optimum process conditions, and the equipment was also used in a solvent recycle mode, to approximate commercial conditions more closely. Appreciable quantities of raffinate and extract were produced in the pilot plant experiments, and were examined with regards to product quality.

Having developed the most important technical data relating to the solvent extraction of synthetic middle distillates, the economics of Syncrude middle distillate extraction with acetonitrile were examined. It was shown that at least in special situations, solvent extraction was a viable alternative to treatment with diesel ignition improvers.

4. RESULTS AND DISCUSSION

4.1 Assessment of Alternative Analytical Techniques

As mentioned in Section 2.3, low-resolution mass spectrometry was selected as the basic analytical technique to evaluate the extraction experiments. It was also indicated there that the loss of light ends was a serious difficulty when attempting to use liquid chromatographic techniques.

The background to the preceding conclusions is that conventional liquid chromatographic methods (27, 30-32) are generally used in the petroleum industry for compositional analysis of higher-boiling fractions than midddle distillates. High Pressure Liquid Chromatography (HPLC; 30, 33-36) was more promising, and this technique was given serious consideration in the present work. However, a number of difficulties were encountered. In particular, the most common (ultraviolet absorption) technique of following the elution of hydrocarbons could not be employed - because of interferences from the solvents - and the refractive index method (37) suffered from baseline setting problems (38) as well as requiring extensive calibration.

In comparison, low-resolution mass spectrometry (28) was trouble-free, and also provided more detailed analyses (Section 2.3).

4.2 Initial Batch Extractions of Syncrude Middle Distillate

Gester (39) has listed the following characteristics of an "ideal" solvent for extracting lubricating oils:

1. High selectivity
2. Good solvent power for the undesirable components
3. Easy solvent recovery (wide difference in volatility between solvent and oil)
4. Low solubility for the desirable oil
5. Sufficient density difference to allow rapid separation of raffinate and extract by gravity
6. Low interfacial tension in order to permit rapid and complete separation into two liquid phases
7. Low cost
8. Ready availability
9. Reasonable temperature of application (preferably treating temperatures such that the oils have low viscosities)
10. Adaptability to a wide range of oils
11. Low toxicity
12. Chemical stability under plant conditions
13. Low freezing point (to avoid complications in cold weather)
14. Noncorrosivity to the usual metals of construction

Most of these characteristics would also be desirable for a solvent used to extract middle distillates. They were taken into consideration by earlier investigators; and hence, the solvents explored in the present work (all of which had been tried out in other applications) automatically satisfied some of Gester's criteria. One could therefore concentrate on measuring - in the initial experiments - five solvent properties of primary interest: distribution coefficients (for aromatics and saturates), selectivity, solvent power and refining power. (These properties will be defined below. They are really characteristic to feed-solvent systems, rather than to the solvents alone.)

Following Perry's Handbook of Chemical Engineering (40), the distribution coefficient, K_a, of the aromatic hydrocarbons may be defined as the weight fraction of aromatics in the extract phase divided by the weight fraction of aromatics in the raffinate phase. Thermodynamically, the partition of the individual chemical species between the solvent-rich and hydrocarbon-rich phases is obtained in terms of mole fractions, rather than weight fractions; but rigourous thermodynamics is not meant for the complex mixtures involved in the extraction of middle distillates. Nevertheless, a thermodynamic approach was utilized in exploring differences between the behaviour of subgroups of saturates and aromatics (e.g. the differences between alkylbenzenes and condensed aromatics); this will be discussed in Section 4.3.4.

Similarly, the distribution coefficient of the saturates, K_s, may be defined as the weight fraction of saturates in the extract phase divided by the weight fraction of saturates in the raffinate phase. The relative separation, or selectivity, between aromatics and saturates in a given experiment may then be characterized by the ratio:

$$S_{a/s} = K_a/K_s$$

K_a, K_s and $S_{a/s}$ are reported in Table 4.1 for each of the exploratory measurements on the various solvents (all of them with Syncrude middle distillate feed).

Kalichevsky and Kobe (25) have suggested another, perhaps simpler definition of selectivity, which is essentially the change in the feed composition divided by the proportion of the feed dissolved. In terms of weight fractions, the definition is:

$$\text{Selectivity (X)} = \frac{X_F - X_R}{E} = \frac{X_E - X_F}{R}$$

where X_F = weight fraction aromatics in the feed
X_R = weight fraction aromatics in the raffinate
X_E = weight fraction aromatics in the extract
E = weight fraction of feed dissolved by the solvent
R = weight fraction of feed in the raffinate

This approach leads to two other, very practical parameters (25):

$$\text{Solvent Power (Y)} = \frac{E}{S}$$

$$\text{and Refining Power (Z)} = XY = \frac{X_F - X_R}{S}$$

where S is normally the volume of solvent employed. (In this work, S was defined as g solvent charged per g feed.)

Table 4.1 contains the Kalichevsky-Kobe parameters, as well as the more conventional distribution coefficients and selectivity values, for each of the solvents evaluated in the exploratory studies. Because of imperfect material balances, the two expressions for the former "selectivity": $(X_F-X_R)/E$ and $(X_E-X_F)/R$ did not give identical results. $(X_E-X_F)/R$, considered the more reliable of the two, is the formula used in Table 4.1. It is denoted by X_2 there.

In addition to giving the experimental results, Table 4.1 also contains some comments on the favourable and unfavourable characteristics of the individual solvents. Evidently, good selectivity is a key property; for instance, selectivity factors $S_{a/s}$ greater than 10 or less than 0.1 should provide virtually complete separation of the appropriate chemical groups if the optimum solvent-to-oil ratio and enough stages are employed. Solvent power (Y) and refining power (Z) indicate whether the desired separation can be effected with a modest quantity of solvent. (Some data on SO_2 as the solvent have been incorporated into Table 4.1, for the sake of comparison.) Solvents such as dimethyl sulphoxide, sulfolane, acetonitrile/CS2, n-formylmorpholine and tetraethylene glycol extracted only small amounts of hydrocarbons. In all four cases the aromatics were extracted preferentially, with high selectivities - but with little promise for commercial success.

Nitroethane extracted hydrocarbons very well (high solvent and refining power) but this solvent was not very selective in aromatics extraction. Similarly, acetone with water, and methanol were eliminated from the search for best solvent due to poor selectivity.

The four most promising solvents were acetonitrile, furfural, N-methyl pyrrolidone and dimethyl formamide. Furfural and N-methyl pyrrolidone were subsequently eliminated, because it was difficult to separate them from the hydrocarbons by distillation.

The role of density is also touched upon in Table 4.1. Other things being equal, the greater the difference in the densities of the extract and raffinate phases, the greater will be the rate of disengagement, and the easier it will be to accomplish complete separation into two liquid phases.

In conclusion, acetonitrile and dimethyl formamide were selected as the "best" organic solvents, for comparative studies with sulphur dioxide. There was some concern, however, that the high boiling point of dimethyl formamide (153°C at atmospheric pressure), which was within the distillation ranges of the middle distillates, would interfere with solvent recovery.

4.3 Evaluation of Acetonitrile, Dimethyl Formamide, and SO_2 in Extracting Aromatics from Syncrude and Suncor Middle Distillates

Syncrude and Suncor middle distillates were extracted at various solvent/oil ratios with:

1) sulphur dioxide at three temperatures: -12, 2, 17°C

2) acetonitrile at three temperatures: 0, 10, 20°C (Syncrude middle distillate was also extracted at 30°C)

3) dimethyl formamide at three temperatures: 0, 10, 20°C

The low temperatures chosen for both organic solvents had been suggested by initial extraction data (Section 4.2). For sulphur dioxide, the aim was to cover with three points a 30°C-wide temperature range; experimental considerations (limited provisions for cooling down the autoclave, see Section 2.4.2) dictated the actual temperatures employed.

4.3.1 Phase Equilibrium Experiments - Raw data, Calculations, Consistency Tests, Phase Diagrams

The raw data from the phase equilibrium experiments are shown in Tables 4.2 to 4.7. In SO_2 extractions, both raffinate and extract phases were fully analyzed, and calculation of the tie-lines was reasonably straightforward. A different procedure was used in acetonitrile and dimethylformamide extractions, as follows.

Raffinates obtained by acetonitrile and DMF extractions contained only up to 6 vol.% solvent. The raffinate phase composition could be readily calculated from the solvent content, the aromatics content of the hydrocarbon constituents, and the density. Although the extract phase was analyzed as well in some experiments, the results of the latter analyses were difficult to use, because the hydrocarbons could not be adequately separated from the solvent. It was therefore decided to determine the total hydrocarbon, solvent and aromatics contents of the extracts by material balance.

A few experimental points were rejected, due to material balance inconsistency, conflict with bulk of the measurements, or failure to fall on acceptable straight lines when plotted according to the method of Bancroft (41) and Hand (42) - an empirical correlation for tie-line data. Appendix III shows that the data of Tables 4.2 to 4.7 are in good agreement with the latter correlation. (The SO_2 extraction results of Tables 4.2 and 4.3 require only minimal further processing to calculate tie-lines; e.g., the aromatics content of the extract phase is merely the product of the total hydrocarbon content and the weight fraction of aromatics in the extract hydrocarbons. The calculations required to convert the raw data of Tables 4.4 to 4.7 to tie-lines are illustrated in Appendix II.)

The resulting nineteen sets of tie-lines (2 feeds x 3 solvents x 3 temperatures plus an additional set of measurements with acetonitrile solvent at 30°C - conducted to allow improved evaluation of the pilot plant data) have been plotted on triangular diagrams, as shown in Figures 4.1 to 4.19. These partial phase diagrams lead to some immediate conclusions.

1. The phase diagrams for the saturates-aromatics - SO_2 pseudo-ternary systems appear to be "bite-type" (43) - Treybal's Type 1 (29) - , i.e., only the saturates and sulfur dioxide form a pair that will not mix in all proportions. This is the most common behaviour in liquid extraction and is suitable to produce high-purity raffinates (here: hydrocarbon streams of low aromatics content and hence high cetane number). On the other hand, such systems tend to limit the purity of the extract. (The lowest concentration of saturates attainable at a given temperature is given by the intersection of the tangent line to the phase diagram, drawn from the SO_2 apex, with the saturates-aromatics side of the triangle.) The latter is an economically important restriction, since processing costs of the extract hydrocarbons (predominantly aromatics) are high. This rules out the use of sulfur dioxide at the high end of the temperature range (Figures 4.3 and 4.6).

2. At certain temperatures, with various feed-organic solvent combinations, only very limited tie-line data have been obtained (see, e.g., Figure 4.8: acetonitrile exctraction of Syncrude middle distillate at 12°C). In order to generate larger parts of the phase diagrams, numerous experiments (at extreme solvent/oil ratios) were carried out beyond those specified in the contract. As a result, it has become clear that both dimethyl formamide and acetonitrile form "band-type" (43), double nonconsolute pseudo-ternary systems with middle distillate saturates and aromatics (see, especially, Figures 4.9, 4.16 and 4.19). The general character of the phase envelopes is probably similar to that shown in Figure 4.20 for a related system: acetonitrile-octyltoluene-n-tetradecane (9). For high-purity (i.e. low paraffin content) extract production, band-type systems have an edge, theoretically, over extraction with SO_2. The quantitative aspects of this will be discussed in Section 4.3.2.

3. As mentioned above, a number of consistency tests have been used to validate the experimental results. For SO_2 extractions, where the raffinate and extract phases were analyzed independently, this included material balance checks. Calculated compositions of the combined feeds (feed + solvent mixtures) theoretically must lie on the tie-lines generated by them; this criterion was closely satisfied for all data retained (Figures 4.1 to 4.6). The data obtained for single-phase systems (Table 4.2, Part II) also show good precision.

One more aspect of the single-stage solvent extraction of middle distillates has been explored: many raffinates and extracts were analysed for traces of sulphur and nitrogen. The results are shown in Tables 4.8 to 4.10. Because of the presence of residual solvent, products from SO_2 extractions were tested for nitrogen content only, and samples from the extractions with organic chemicals only for sulphur content. On comparing Tables 4.8 to 4.10 with Table 2.1 one concludes that both nitrogen and sulphur compounds tend to be extracted, but acetonitrile is effective for sulphur removal only at very high solvent-oil ratios.

4.3.2 Extraction Process Design for Each Solvent, Solvent Selection for Pilot Plant Studies

As discussed in Section 4.3.1, some conclusions concerning the potential of various solvents could be derived merely from an inspection of the partial phase diagrams. More precise assessments involved the calculation of the number of theoretical stages that would be required to produce raffinates and extracts of specified purity by single-solvent countercurrent extraction. The graphical calculation method of Hunter and Nash (44) was employed throughout; the results will be discussed in terms of the constructions shown in Figures 4.21 to 4.32.

4.3.2.1 Sulphur Dioxide Extractions

It was mentioned in Section 4.3.1 that at 17-18°C the phase behaviour relations are such as to rule out the production of extracts containing low concentrations of aromatics, with SO_2 as the solvent. (Literature references (2) also indicate that operating temperatures in the range of -35 to 0°C are more appropriate when SO_2 is employed to extract middle distillates). At the lower temperatures (-12°C and 2°C) the outlook was better and the number of extraction stages required could be estimated; but since only parts of the binodal curves and associated tie-lines had been determined experimentally, the Syncrude data were extrapolated slightly and the Suncor calculations were based on combined Syncrude-Suncor data. (Sherwood's procedure (45) was used to extrapolate the tie-lines. Combination of the Syncrude and Suncor data was possible because of the great similarity between the binodal curves and tie-lines. This may be seen by superimposing Figures 4.1 and 4.4, as well as Figures 4.2 and 4.5).

Figures 4.21 and 4.22 show the combined phase envelopes and Hunter-Nash constructions for the extraction of Suncor middle distillate with SO_2. One or two theoretical plates suffice to achieve an aromatics content of 20 wt.% in the raffinate, at solvent/oil ratios of 1.7 or less (wt/wt). However, extract quality is not very satisfactory, especially at 2°C (cf. Section 4.3.1). The process design for Syncrude middle distillate feed (40 wt.% aromatics versus 30 wt.% for Suncor) has given similar results; the tie-line extrapolations and Hunter-Nash constructions for Syncrude feed are shown in Figures IV.1 and IV.2 of Appendix IV.

4.3.2.2 Acetonitrile Extractions

Figures 4.23 to 4.26 are Hunter-Nash constructions for acetonitrile extractions of Syncrude and Suncor middle distillates at 0°C and 20°C. They indicate that it will be relatively easy to produce raffinates containing only 20 wt.% aromatics* and extracts rich in aromatics (95 wt.%). 2-5 theoretical stages and solvent-oil ratios ranging from 1.5 to 2.7 wt/wt will suffice, the number of plates and solvent-oil ratios being lower for Suncor feed and at the higher temperatures. (This led to additional experiments at 30°C, the results of which have been incorporated into Section 4.3.1.)

For Suncor middle distillate, a Hunter-Nash construction was also carried out at 10°C, with results intermediate between the 0°C and 20°C ones (see Figure IV.3, Appendix IV). Syncrude tie-line data with acetonitrile solvent at 12°C did not cover a sufficiently wide range to carry out the process design calculations, but otherwise they were very similar to the 20°C results, suggesting a solvent-oil ratio of 2.0 wt/wt and 5 theoretical plates. The latter conditions later turned out to be exactly the same as required at 30°C (Figure 4.27); so, the acetonitrile extraction process does not seem strongly temperature dependent in the 10-30°C range.

*At the time of these design calculations it was assumed that the aromatics level had to be reduced to 20 wt% in order to achieve a cetane number of 40. Subsequent work (Section 4.3.3) indicated that significantly higher aromatic contents were still acceptable.

4.3.2.3 Dimethyl Formamide Extractions

At first glance, the dimethyl formamide-middle distillate partial phase diagrams (Figures 4.14 to 4.19) appear to be similar to the corresponding acetonitrile-middle distillate results (Figures 4.7 to 4.9 and 4.11 to 4.13) but on close examination we note that the acetonitrile system tie-lines slope much more steeply. Hunter-Nash constructions (among other calculation techniques, a number of which are described in Ref. 29) make it possible to "translate" the differences into process parameters. It was assumed throughout these calculations that the objective was to produce raffinates containing 20 wt.% or less aromatics and extracts containing 95 wt.% or more (cf. Section 4.3.2.2). The somewhat surprising conclusion was reached that whereas in one way DMF was superior to acetonitrile: for Syncrude middle distillate it could achieve the required separations (Figures 4.28 to 4.30) with less solvent and a smaller number of stages than acetronitrile (Figures 4.23 and 4.24) - in another way it was inferior: DMF could not produce the required streams from Suncor feed at 20°C (Figure 4.31).

4.3.2.4 Solvent Selection for Pilot Plant Studies

As discussed in Section 4.3.1, the middle distillate-solvent pseudo-ternary phase diagrams offered important guidance as to solvent selection - even without design calculations. It was mentioned there that acetonitrile and dimethyl formamide formed double nonconsolute pseudo-ternaries with middle distillate saturates and aromatics, promising extracts of very low saturates content. Indeed, the process designs of Sections 4.3.2.1 to 4.3.2.3 have shown that acetonitrile and DMF will usually yield 95 wt% or more aromatics in the extract hydrocarbons without much difficulty. Even at the lowest temperature explored in the present project (-12°C), it did not seem possible to reduce the saturates content of extracts below 10 wt% with sulfur dioxide as the solvent. Operating at lower temperatures still, was tentatively* considered too expensive. The economic penalty for

*The detailed economics of SO_2 extraction have not been explored in the present work.

leaving an appreciable quantity of saturated hydrocarbons in the extract stream can be substantial, if the extract is to be refined by severe hydrogenation. Therefore, the organic solvents, which offer better selectivity, were immediately assumed to have better prospects.

Choosing between acetonitrile and DMF was more difficult. As discussed in Section 4.3.2.3, dimethyl formamide will sometimes achieve the required separations with less solvent and a smaller number of extraction stages than acetonitrile. By and large, however, the distribution coefficients, selectivities, solvent and refining powers of the two organic chemicals, are similar at the temperatures of interest (Table 4.1). The decisive difference was that, owing to its much higher boiling point, DMF was difficult to separate from the light ends of the feed. Also, the raffinate phases produced with DMF had higher solvent contents to start with. Perhaps DMF would be an excellent solvent for middle distillates of higher initial boiling point; but for the experimental program conducted under the present contract, acetonitrile seemed superior. The latter chemical was therefore selected for the pilot plant studies and further evaluation.

4.3.3 Subgroup Selectivity Effects

As mentioned in Section 2.3, one advantage of using mass spectrometry was the detailed analytical information generated on feed, raffinate and extract hydrocarbons. It was suggested that there could be differences between the selectivities for different subgroups of hydrocarbons, e.g. alkylbenzenes and multi-ring aromatics, and that this could have a significant influence on product quality. Indeed, at the Petro-Canada Products (formerly Gulf Canada) R&D Centre, correlations between cetane number and mass spectrometric breakdown have been used routinely for several years (46, 47). It is well known, for instance, that paraffins have a more favourable influence on cetane number than, say, condensed cycloparaffins. Yet, up to here, the present report has been referring to both subgroups only as "saturates".

In order to understand subgroup fractionation - and the relationship between composition and cetane number - better, single-stage and some pilot plant extraction data have been examined more closely. The aim* was to detect differences between the distributions of subgroups of saturated and aromatic hydrocarbons in the raffinate and extract phases (paraffins, non-condensed cycloparaffins, condensed cycloparaffins, alkylbenzenes, and condensed aromatics). Only the most promising temperatures were considered for each middle distillate-solvent pair, as follows:

Syncrude-Sulfur Dioxide	Equilibria	at	-12°C
Suncor-Sulfur Dioxide	"	"	-12°C
Syncrude-Acetonitrile	"	"	20°C
Suncor-Acetonitrile	"	"	20°C
Syncrude-Dimethyl Formamide	"	"	20°C
Suncor-Dimethyl Formamide	"	"	0°C
Syncrude-Acetonitrile	Pilot Plant Extraction Data	at	20°C
Suncor-Acetonitrile	" "	" "	20°C

The reader will recall that extract compositions for middle distillate-organic solvent systems were calculated by material balance. This required high analytical and experimental accuracy when dealing with subgroups. Experiments No. 9 and 10 of Table 4.4 (extractions of Syncrude middle distillate with acetonitrile) did not measure up to this standard and were excluded. Similarly, only the highest quality pilot plant data were suited to this more detailed analysis, hence three Suncor-Acetonitrile and two Syncrude-Acetonitrile runs at 20°C were specially selected for the subgroup study (Section 4.4.4). The single-stage data on which the calculations have finally been based are given in Tables 4.12 to 4.14, and the corresponding feed analyses** in Table 4.11.

The subgroup selectivity effects can be observed by comparing the distributions of saturates and aromatics in the feed to their distributions in the raffinate or extract hydrocarbons.

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* The broader objective was to use predicted cetane number - not just its rough indicator, the aromatics content - as a measure of raffinate quality.

**These analyses refer to slightly different samples from the ones characterized in Tables 2.1 and 2.2

(Except for the SO_2 experiments, extract compositions were calculated by material balance. The calculations were similar to those reported in Appendix II for an acetonitrile extraction of Syncrude middle distillate. Small concentrations ot saturates present in the extract could not be computed with any degree of precision.) Tables 4.15 to 4.17 show the paraffin and non-condensed cycloparaffin contents of raffinates with respect to the total saturates, and their alkylbenzene content with respect to the total aromatics. Referring to the feed analyses, we note minimal fractionation with SO_2 as the solvent, but subgroup separations seem significant with acetonitrile and dimethyl formamide. Large solvent/oil ratios favour subgroup fractionation phenomena. (The latter type of data have not been obtained with SO_2 as the solvent; hence the distinction between sulphur dioxide and the organic solvents is not well established.)

With acetonitrile, the major result of subgroup selectivity is the decrease of the alkylbenzene content of raffinate aromatics, but there is also a noticeable increase in the paraffin content of the saturates - compared to the feeds. With DMF, the effects are similar, but their relative magnitudes are reversed. In both cases, one consequence will be higher cetane numbers of the raffinates than in the absence of subgroup selectivity, see below.

From a practical point of view, the relationship between raffinate composition and cetane number is the most important, since other fuel specifications are easier to meet than ignition quality (Section 4.4.3.2). At the Petro-Canada Products (formerly Gulf Canada) Research and Development Centre, correlations between cetane number and mass spectrometric analysis were originally obtained by regressing measured ASTM cetane numbers for approximately 150 samples against the concentrations of paraffins ($Z = +2$), mono-cycloparaffins ($Z = 0$), condensed dicycloparaffins ($Z = -2$), condensed polycycloparaffins ($Z = -4$), alkylbenzenes ($Z = -6$), benzo-cyclo- and benzo-dicycloparaffins ($Z = -8, -10$), naphthalenes ($Z = -12$) and "other aromatics" ($Z = -14, -16$, etc.) found in each sample (46,47). In the present work, an improved correlation has been used - thought to be applicable to a wider variety of diesel fuels, and incorporating molecular weight dependence. This new model generally agreed well with the published properties of individual hydrocarbons (48), and has also been corroborated by two observations:

(1) When comparing predicted cetane numbers with values that one would expect from the carbon/hydrogen ratio, using a published correlation for virgin distillates and commercial fuels (49), the discrepancies are typical of diesel fuels derived from Canadian tar sands (50).

(2) The lower blending cetane number of alkylbenzenes (51), compared to naphthalenes, agrees with the view that benzene rings in synthetic distillates tend to be highly substituted with alkyl groups and that this depresses the cetane number (50).

The most direct confirmation of the applicability of our cetane number correlation to Syncrude and Suncor raffinates would come from comparing measured and calculated cetane numbers. Unfortunately, the few production samples of Syncrude raffinate that have been cetane rated do not provide any conclusive evidence. Table 4.18 indicates that for Syncrude raffinates - which are, after all, quite different from the usual diesel fuels, whether "conventional" or "synthetic" - the correlation underpredicts cetane number by 2-1/2 units, on the average. Yet, when compared to the usual standard error of our correlations (1.7 units), the increased discrepancy has low statistical significance. Also, incorporation of the Syncrude raffinate results into our data base and recalculating the regression coefficients has had little effect.

It is concluded that the cetane number correlation used in this work is a suitable predictor of product quality, at least for preliminary process design and economic evaluations. It was employed in the following manner:

Subgroup concentrations in a given raffinate, with respect to the total saturates and total aromatics, were compared to concentrations that would have been obtained in the absence of subgroup fractionation. (For example, referring to Tables 4.6 and 4.17, it is easily calculated that for Syncrude/DMF Experiment No. 211, the paraffin hydrocarbon content of the raffinate would have been only 22.50 wt%, instead of 27.44 wt%, had all saturates behaved the same way.) Cetane numbers were then

calculated for both the "real" and "recalculated" (no subgroup fractionation) raffinates. The outcome of these computations for single-stage extractions has been the conclusion that subgroup selectivity has little effect on SO_2 extractions, (cf. p.23), but that with acetonitrile or DMF as solvents, subgroup fraction may result in a two cetane number increase, in addition to the beneficial effect of overall aromatics removal.

Further details concerning the methods of calculation, and their results, are given in Section 4.4.4, where the pilot plant data are examined.

4.3.4 Computer Simulation of Tie-Line Data

In view of the significant, beneficial effects of subgroup fractionation, an attempt was made to fit a thermodynamic model to the acetonitrile single-stage extraction data. Such a model would have permitted computerized process design calculations - allowing for subgroup selectivity and opening up avenues for process optimization -, and would have also aided in material balance reconciliations, i.e. in a fuller appreciation of the significance and weak points of the multi-stage extraction data.

Computations were performed with the aid of the Simulation Sciences Inc. PROCESS™ Flowsheet Simulator (52). A simple, regular solution model (52,53) was adopted for activity coefficient calculation - lack of binary data and computer programs to fit tie-lines have precluded a more sophisticated attack. Regular solution theory is, in fact, a frequently used technique (29) for predicting the distribution in liquid extraction, at least when the deviations from ideality are not caused by hydrogen bonding. (Actually, acetonitrile does form three-dimensional networks of hydrogen bonds, but the linkages are quite weak. In cases like this, it is sometimes still possible to use the Scatchard-Hildebrand equation (29,52), with empirically assigned solubility parameters - albeit the theoretical foundations disappear.)

Many details of the thermodynamic model used and step-by-step improvement of the input parameters have been described in an interim report (54). Here, it will suffice to say that simulation of individual tie-lines has been found quite feasible*, but that the model was not nearly accurate enough over a range of concentrations/tie-lines (Table 4.19).

It would appear that if the thermodynamic approach will be pursued, one should consider models other than regular solutions. Dr. A.D. Pelton, Co-Director of the Ecole Polytechnique's Centre for Research into Computational Thermochemistry (Montreal) has kindly offered to examine the tie-line data and estimate whether they could be fitted, using computer techniques available at the latter research centre. (This would be no trivial task, in light of the difficulties encountered to-date, and because of the pooling of groups of hydrocarbons.) But since many other aspects of the acetonitrile extraction process also deserve further attention - perhaps more than the subgroup selectivity effects, which have been explored quite thoroughly -, it was decided jointly with the Scientific Authority not to conduct additional thermodynamic studies under the present contract.

4.3.5 Batch Simulation of Three-Stage Continuous Countercurrent Extraction with Acetonitrile at 20°C, Syncrude Middle Distillate Feed

Prior to embarking on a series of pilot plant tests of continuous countercurrent extraction (the most realistic "affordable" method for evaluating solvent extraction), it was desirable to attempt a batch simulation of the continuous process (29). Separatory funnels were employed, as described by Treybal; diagrams of the continuous process simulated and the batch cascade flow chart are given in Figure 4.32. Table 4.20 shows the approach to steady state, as monitored by density measurements, and the resultant raffinate and extract compositions.

*Liquid-liquid equilibrium calculations had to be replaced by a sequence of steps: 1) Liquid-liquid equilibrium; 2) Flashing off excess solvent from the raffinate; 3) Returning the vapours to the extract.

A 2:1 wt/wt solvent-oil ratio was simulated. Plotting the resultant raffinate and extract phase compositions on the appropriate phase diagram and carrying out a Hunter-Nash construction showed a separation equivalent to four theoretical plates (Figure 4.33). There was no evident obstacle in the way of proceeding with the pilot plant tests.

4.4 Pilot Plant Evaluation of the Acetonitrile Extraction of Synthetic Middle Distillates

4.4.1 Survey Runs with Syncrude and Suncor Middle Distillates

In order to generate more realistic operating data for assessing and costing the solvent extraction of middle distillates - especially with acetonitrile as the solvent - twenty-three pilot plant survey runs were carried out. These experiments were conducted over approximately 8 to 16 hours each, allowing sufficient time to reach stationary conditions. Various temperatures, solvent-oil ratios and feed rates were explored. Raffinate phase samples collected over the last hour or two of each run were analyzed in the usual manner (Section 2.3) and the corresponding extract phase compositions were obtained by material balance calculations, similar to the example given in Appendix II.

Eight of the above runs have been selected for more detailed study, because of their steady-flow rates, good mass balance and consistency with the corresponding equilibrium phase diagrams. The operating conditions and analytical results for these eight runs are shown in Table 4.21, and for the fifteen runs set aside, in Table V.1 of Appendix V.

Raffinate and extract compositions derived from the data of Table 4.21 have been plotted on appropriate phase diagrams - Figures 4.34 to 4.36. Since all these experimental points fall on the binodal curves, Hunter-Nash constructions could be used to calculate the height equivalent to a theoretical stage (H.E.T.S.) in any particular survey run. Specifically, in the most successful pilot plant test (Runs 20-23 of Table 4.21) this evaluation (Figure 4.37) indicated approximately 2.5 theoretical plates, or an H.E.T.S. of 6-7 feet. Although the efficacy of the extraction column was below expectations (cf. Section 2.4.4)

the equipment was suitable to produce raffinates meeting basic tests (Table 4.22), as well as for product evaluations on a larger scale (Tables 4.23 abd 4.24). However, at the (apparently) optimal operating conditions of 20°C, 3.3:1 solvent- oil ratio (wt/wt) and a feed rate of 180 mL/hour, the aromatics content of the extract hydrocarbons did not greatly exceed 80 wt%.

4.4.2 Pilot Plant Studies in "Production Mode"

Since the extraction of Syncrude middle distillate with acetonitrile at 20°C, nominally 200 mL/hour feed rate and 3:1 wt/wt solvent-oil ratio, produced the raffinate of lowest aromatics content, these operating parameters were chosen for the more demanding "production run", involving solvent recirculation. The main objectives were to ascertain that the raffinate hydrocarbons would have a cetane number over 40 and to observe the effect of impurities accumulating in the recycled solvent.

Prior to starting solvent recirculation, the pilot plant was operated in the fresh solvent mode for 28 hours, to reach steady state conditions. During this time period the solvent distilled off from the raffinate and extract phases was collected and set aside. In the next phase of the "production run", this distillate and all further distillates obtained from continuous fractionation of the pilot plant effluents were recycled as solvent for the extraction. This recycle operation was maintained for 96 hours. It became evident though, that the quality of the raffinate was deteriorating (the aromatics content built up to almost 30 wt%) as fresh solvent was replaced by recycled acetonitrile. This was attributed to the accumulation of hydrocarbons in the solvent stream (incomplete separation of acetonitrile from the middle distillate). Therefore, it was necessary to discontinue the solvent recirculation and to return to fresh acetonitrile addition for 72 hours. The raffinates from the various phases of the "production run" were then combined into a single, 25-litre sample, containing 24.73 wt% aromatics (75.27 wt% saturates). Virtually all traces of solvent had been removed by distillation, assisted with stripping nitrogen. Detailed characterization of this product will be discussed in Section 4.4.3, but it is notable that its cetane number was as high as 42.2. The aromatics content of the recovered extract hydrocarbons was 91.5 wt%, so both streams obtained were reasonably uncontaminated, in spite of the difficulties encountered with solvent recirculation.

4.4.3 Product Evaluations

4.4.3.1 Product Specifications

Diesel and aviation turbine fuel specifications from the Canadian General Standards Board and the ASTM Book of Standards were referred to and are partially reproduced in Appendix VI.

4.4.3.2 Characterization of Raffinates from Pilot Plant Survey Runs

In addition to determining the aromatics contents of the raffinate hydrocarbons, reported in Tables 4.21 and Appendix V, inspection data were obtained on 14 raffinates from the pilot plant survey runs (Table 4.22). Referring to the product specifications given in Appendix VI, it is seen that cetane number is the only quality requirement that may not be easily met. As discussed in Section 4.4.4, a cetane number of 40 can, in fact, be fairly easily attained, because of favourable subgroup fractionation effects.

4.4.3.3 Characterization of the Pilot Plant "Production Run" Composite Raffinate

Results of the specification testing of this raffinate are given in Table 4.23. This product could be described as a high-quality diesel fuel; there is no indication that the extraction process creates difficulties. Subsequently, a portion of the above raffinate was fractionated in a 25-theoretical-plate spinning band column, yielding 84.4 wt% of a fuel with a final boiling point of 300°C. The inspection data shown in Table 4.24 indicate that it would be easy to produce from Syncrude raffinate specification Jet A aviation fuel (by lowering the end point).

4.4.4 Subgroup Selectivity Effects

The finding that different subgroups of the major groups of hydrocarbons (saturates and aromatics) behave differently in terms of their distribution between the raffinate and extract phases, has been discussed in Section 4.3.3. It was also suggested there that this would have a significant bearing on raffinate cetane numbers. However, the pilot plant data were better suited to examine these effects, since multiple contact tended to enhance them.

As mentioned in Section 4.3.3, two Syncrude-acetonitrile and three Suncor-acetonitrile pilot plant experiments at 20°C have been selected for subgroup selectivity calculations. The basic experimental data for these runs have been given in Table 4.21. Additional analytical information is shown in Table 4.25. The data of the latter table exhibit appreciable subgroup selectivity effects.

To evaluate the impact of subgroup selectivity effects on product quality (cetane number), a similar approach was used as in Section 4.3.3: quality parameters were computed for the actual raffinate breakdowns, and for recalculated compositions which eliminated fractionation with respect to subgroups. The sample calculations that follow illustrate the procedure.

Let us consider pilot plant experiment No. 20-9 (extraction of Syncrude middle distillate with acetonitrile at 20°C, nominal solvent/oil ratio = 1.5 vol/vol, approximately two theoretical stages). The relevant mass spectrometric analysis (more detail is available, but is not used in the cetane number correlation) is shown in Column 2 of Table 4.26, and Column 5 gives the subgroup concentrations with respect to total saturates and total aromatics in the raffinate. Column 6 shows concentrations of the same subgroups in the feed saturates and aromatics. Using the values of Column 6, the raffinate saturates and aromatics can then be redistributed - leaving the overall aromatics content as determined, but cancelling out the subgroup fractionation that took place going from feed to raffinate. Column 3 gives the resulting, hypothetical raffinate breakdown. Product quality predictions based on Column 2 and Column 3 can be compared, showing the "practical consequences" of subgroup selectivity. For experiment No. 20-9, the cetane number prediction for the actual raffinate is 38.3, but it is only 36.4 for the hypothetical composition, i.e. without subgroup fractionation.

By means of material balance calculations, it is also possible to assess whether significant further improvement of product quality could be achieved by enhancing subgroup selectivity - beyond what has been observed. Continuing our example calculations, the observed flow rates of 258.6 g/h feed, 381.7 g/h

solvent and 212.6 g/h raffinate imply that there are only 2-3 g/h saturates in the extract. Redistribution of this small quantity with respect to subgroups will have only a modest effect on raffinate quality. Comparing Columns 5 and 6 of Table 4.26, it is also seen that considerable subgroup selectivity differences have already affected the distribution of heavy aromatics (naphthalenes, "other" condensed aromatics), and it will be difficult to accomplish further improvement along the latter lines. (Also, here again, only small quantities are involved.) The most promising way of achieving higher cetane number at the same aromatics level would therefore be to extract more alkylbenzenes and less benzocycloparaffins (including benzo-dicycloparaffins). Here too, there are material balance limitations. If the alkylbenzenes/total aromatics ratio is reduced to 0.3 in the raffinate, with a corresponding increase in the benzocycloparaffins/aromatics ratio, the extract will contain approximately four times as much alkylbenzenes as benzocycloparaffins. Further enrichment of the extract in alkylbenzenes does not seem practical. As for this prospective, "improved" raffinate, its cetane number was estimated at 39.3 - only a one number increase compared to the actual raffinate from experiment No. 20-9.

The picture is similar when the solvent is dimethyl formamide. In experiment No. 210 (Tables 4.14 and 4.17) for example, there is room to improve the raffinate both by increasing the paraffins/saturates ratio and by (substantially) decreasing the alkylbenzenes/aromatics quotient. However, if the saturates content of the extract were reduced to, say, 5 wt.%, by multistage extraction, then saturate subgroup selectivity would have little effect on the raffinate cetane number. Alkylbenzenes removal at a constant total aromatics level seems to have better potential, but it is unlikely that the predicted cetane number could be improved much beyond the value of 40.7 calculated for DMF experiment No. 210.

It is concluded that even when subgroup selectivity has been fully exploited, the aromatics content of diesel fuels would have to be reduced to approximately 26 wt.% in order to achieve a calculated cetane number of 40. (If our correlation underpredicts raffinate cetane numbers, and the bulk of the alkylbenzenes have been extracted, 30 wt.% aromatics may be permissible in the raffinates.)

Table 4.27 summarizes the assessment of subgroup fractionation effects in terms of predicted cetane numbers - for all the experiments evaluated in this manner. This includes raffinate samples collected at various stages of the "production run" (Sample Nos. 24-004 through 24-052). The results are also given graphically in Figures 4.38 to 4.40. Once the subgroup selectivity effects have been eliminated, the cetane number correlation becomes linear in the aromatics content (except for molecular weight dependence); separate straight lines represent Syncrude and Suncor raffinates adjusted to feed subgroup breakdowns.

Because of subgroup fractionations of varying intensity, the correlation between aromatics content and predicted cetane number for the "real" raffinates shows appreciable scatter. Figure 4.38 confirms that the performance of sulphur dioxide does not benefit greatly from subgroup selectivity effects (Section 4.3.3); beyond this it is difficult to discriminate between solvents, or between single-stage and pilot plant results (Figure 4.40). The beneficial effects of subgroup fractionation appear to be stronger with Syncrude than with Suncor middle distillate feed (Figure 4.39); the reasons for this have not been explored.

4.5 Economic Assessment of the Solvent Extraction of Middle Distillates

4.5.1 Introduction

To put the solvent extraction process into the best possible light, an advantageous situation is required. The application with, perhaps, the most promise would be the Syncrude operation at Mildred Lake, Alberta.

The Syncrude plant has on site diesel requirements of approximately 780 bbl/day, to operate heavy earth moving equipment. The current practice is to purchase finished commercial diesel fuel, supplied from refineries in Edmonton. The delivered cost of this diesel fuel is roughly 35¢/L or $15.8 MM per year in additional operating cost. In contrast, Syncrude can produce middle distillate for about crude cost, or roughly 12¢/L ($10.4 MM/year savings). However, the site-produced middle distillate is only 32 CN* and this ignition quality is too low for medium-speed diesel applications.

4.5.2 Processing

Assuming that the desired ignition quality is 40 CN, the Syncrude-produced diesel must be treated or upgraded. The solvent extraction process is proposed for this purpose, and fits well in this case, because the extract aromatics could be "buried" back into the crude production. The competing economic case will be the use of Diesel Ignition Improver (typically octyl nitrate), to achieve 40 CN from 32 CN base-stock. The estimated treat rate is 0.6 vol.%, based on the response curves of chemical suppliers. Both of these cases require a distillation system to recover middle distillate from the gas oil hydrotreater product at Syncrude. Figure 4.41 shows a simplified Syncrude operation overview, with the solvent extraction process shown added on.

The Syncrude processing system hydrotreats only two crude fractions from coker product. One fraction is a C_4 to 193°C boiling point cut and the other fraction is a total bottoms, boiling from 194°C to 524°C. A typical diesel could

*Cetane Number

be cut at 194°C to an end point of about 340°C. This would give good seasonal cloud and pour point, as well as provide good feedstock for a solvent extraction process. Figure 4.42 shows an example design for a 1000 bbl/stream day unit. This would furnish sufficient on-site diesel, with a 300 day/year on-stream factor. Table 4.28 lists the process assumptions for 1000 bbl/stream day diesel production, with a target quality of 40 CN.

4.5.3 Economic Assessment

In order to conduct an economic assessment of the solvent extraction process, the process flow sheet of Figure 4.42 was developed and all process equipment was costed out by the Guthrie method. All costs were developed from actual U.S. Gulf Coast (1968) installed costs. Table 4.29 lists the process equipment and gives individual cost data, and Table 4.30 is a cost summary.

The economic comparison or feasibility study assumes that either diesel ignition improver or solvent extraction will be chosen for the production of on-site diesel.

CASE 1: Ignition Improver

From the cost information supplied in the tables, the following economics are presented on a ¢/L basis. All costs are 3rd Quarter 1986 Canadian dollars.

Capital Equipment (15 year Amortization @ 10%)	=	0.5
Operating Cost	=	5.0
Materials Cost (Ignition Improver @ $2.75/lb)	=	3.2
Processing Cost		8.7
Raw Material Cost		12.0
Total On-Site Cost		20.7 (vs 35¢/L)
Net Cost Savings		14.3¢/L
DCF ROI (over 15 years based on 6% inflation and a constant savings margin)		2100%

CASE 2: Solvent Extraction

Again, all costs are converted to a ¢/L basis, using 3rd Quarter 1986 Canadian dollar data.

Capital Costs (15 year Amortization @ 10%)	= 1.36	
Operating Costs	= 13.32	
Processing Cost	14.68	
Raw Material	12.00	
Total On-Site Cost	26.68	(vs 35¢/L)
Net Cost Savings	8.32¢/L	
DCF ROI (over 15 years, based on 6% inflation and constant savings margin)	430%	

Comparing the above two cases, it would seem that a substantial advantage is enjoyed by straight treatment with ignition improver (NPV* = $72 MM versus $36 MM in Case 2). However, the solvent extraction route provides clear cetane fuel at 40 CN and would not produce a significant dependence on a cheap source of ignition improver. Projecting an increased diesel demand and upward pressure on commercial CN levels, ignition improver might easily increase in price. The solvent extraction route, therefore, offers some strategic advantage. For the Syncrude application, solvent extraction is a viable alternative.

Other applications of solvent extraction as a means of diesel fuel upgrading will depend heavily on an economic end use of extracted aromatics. This would require further study and is recommended as a future task.

*NPV - Net Present Value

5. CONCLUSIONS

5.1 A solvent extraction process to separate the aromatic and saturated hydrocarbon components of synthetic middle distillates seems technically feasible.

Specification diesel and jet fuels can be produced by this means.

5.2 A rather thorough evaluation of SO_2 and eleven organic solvents (containing additives such as water in a few cases) has left liquid sulphur dioxide the leading contender to effect the above separation.

5.3 Among the organic solvents studied, acetonitrile has been the most promising. It appears to form double non-consolute pseudo-ternary systems with middle distillate saturates and aromatics; this suggests that extracts of high "purity" (95 wt% aromatics content or more) can be readily obtained with acetonitrile, at room temperature. Raffinate quality is also very satisfactory.

5.4 When acetonitrile is distilled off from the extract, some of the hydrocarbons contaminate the distillate. This difficulty must be overcome before acetonitrile extraction can become a viable process.

5.5 Low-resolution mass spectrometry - the most successful analytical method for determining the saturates and aromatics contents of feed, raffinate and extract - has provided additional information on the separation process. Subgroup selectivity effects, such as preferential extraction of alkylbenzenes compared to benzocycloparaffins, often improve diesel fuel quality by two Centane Numbers or more.

6. RECOMMENDATIONS

6.1 Literature data on the sulphur dioxide extraction of middle distillates should be reviewed in conjunction with the present project's results, to estimate the economics of employing this solvent at low temperature.

6.2 If the economics of SO_2 extraction seem favourable, a pilot plant should be constructed, to generate further technical and economic data on this process.

6.3 The feasibility of acetonitrile extraction of synthetic middle distillates should be further investigated. Improved separation of acetonitrile from the raffinate may be possible just by adding a small amount of water prior to fractionation.

6.4 Fractions of synthetic middle distillates obtained by extraction with organic solvents, should be used to elucidate the relationships between fuel quality and composition.

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Appendix VI: Product Quality Requirements as Formulated under ASTM and CGSB Specifications

Standard Specification VI.1: Canadian General Standards Board, Diesel Fuel, CAN2-3.6-M83

Standard Specification VI.2: Canadian General Standards Board, Standard for Turbine Fuel, Aviation - Jet A, CAN2-3.23-M81

Standard Specification VI.3: Aviation Turbine Fuels, ASTM D1655-85a

Standard Specification VI.4: Diesel Fuel Oils, ASTM D975-81

TABLE 1.1

Solvents Considered to Extract Aromatics from Middle Distillates - Literature Study

Solvent	Boiling Point °C	Density g/cc at Ambient Temp.	Water Added?	Tentative Evaluation* of Chances of Success	Other Comments*	References
Sulphur Dioxide	-10	1.43	No	Good	Unlike furfural, this solvent is better suited to middle distillates than to lubricating oil refining.	1,2
Furfural	162	1.16	Sometimes	Promising, but may have to be used in combination with other solvents.	Recommended for broad-range fractions, on theoretical grounds. Used with furfuryl alcohol in the REDEX Process.	2,3,4,5,6, 12
Methanol	65	0.79	Yes	Promising solvent, but probably must be used in combination with co-solvents (CS_2 - Ref.7, Sulfolane - Ref. 8).		7,8
Acetonitrile	82	0.78	No	Insufficient information has been published to form an opinion.	May have to be used in combination with a cosolvent, such as CS_2	9
Ethylene Glycols (DEG, TEG)	244-290	1.13	Sometimes	Fair. Appear to be more suitable to extract naphthalene derivatives and tricyclic aromatics than alkylbenzenes.	Better solvents are available (probably).	10,11,12
Pyridine	115	0.98	Yes	Good. Pilot plant studies have been successful. High selectivity, good solvent power.	Low-boiling-point solvent, thermally and chemically stable, no corrosion problems.	13,14

*The evaluations and comments in this table are based on published information. Conclusions reached in the present project will be discussed in subsequent sections.

TABLE 1.1 (Continued)

Solvent	Boiling Point °C	Density g/cc at Ambient Temp.	Water Added?	Tentative Evaluation of Chances of Success	Other Comments	References
Sulfolane	285	1.26	Perhaps a small quantity	Good for lower boiling fractions, increasingly unlikely as the boiling point of the aromatics approaches 300°C.	Less suitable for naphthaline derivatives than for alkylbenzenes. Sulfolane-methanol-water mixtures have been suggested to extract aromatics from kerosene.	8,12,15
Dimethyl Formamide	153	0.94	Sometimes	Excellent. Extraction of 180-350°C and 240-350°C crude fractions has been pilot planted.	Addition of water greatly improves the selectivity, but may cause solvent loss and corrosion problems through hydrolysis. A second solvent, such as heptane may be added to avoid water injection. Also used in the REDEX Process.	3,16,17,18, 19,20
Tetrahydro-Furfuryl Alcohol	178	1.05	Yes	Good. (On the authority of Marathon Oil workers who published a paper on the REDEX Process.)		3
Furfuryl Alcohol	171	1.13	Yes	Good. (On the authority of Marathon Oil workers, as above.)	Used with furfural	3
Methyl and Ethyl Carbamate	177-180	0.98-1.14	No	Selectivity and solvent power are adequate, but not outstanding.	Recommended by some Russian authors on grounds of ready availability, low toxicity, non-corrosiveness, easy regeneration, process operability near ambient temperatures.	12,21,22

TABLE 1.1 (continued)

Solvent	Boiling Point °C	Density g/cc at Ambient Temp.	Water Added?	Tentative Evaluation of Chances of Success	Other Comments	References
N-Methylpyrrolidone	202	1.02	Yes	Not good. Process would have to be optimized by adding just the right amount of water to the solvent.	Russian authors have suggested that the cost and availability of NMP would pose problems.	12,19,22, 23
Propylene Carbonate	242	1.21	Yes	Good selectivity and solvent power, but no information has been published on the economics of this solvent.		12,22
Morpholine	128	1.00	Yes	Poor. Selectivity and solvent power are unimpressive.		12
Dimethyl Sulfoxide	189	1.10	Sometimes	Poor. Furfural was found to be a better solvent in a comparative study.		6
N,N'-Dimethyl-Imidazolidone	104 @ 15 mm	Not Reported	Yes	Insufficient information is available to judge.	Solvent is claimed to be non-corrosive, of low toxicity, and thermally and hydrolytically stable.	24

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TABLE 2.1

MIDDLE DISTILLATE CHARACTERIZATION

Analyses		Syncrude M.D	Suncor M.D.
Density @ 15°C	ASTM D4502	0.8621	0.8498
API Gravity		32.6	34.9
Viscosity @ 25°C	ASTM D445	2.7	2.88
(cSt) @ 40°C		2.1	2.14
Pour Point, °C	ASTM D97	-66	-60
Aniline Point, °C	ASTM D611	43.6	52.7
Sulphur, ppm	ASTM D4294	145	619
Conradson Carbon, wt%	ASTM D189	0.01	N/A
Nitrogen, ppm	ASTM D3431	52.5	75
Water, ppm	ASTM D1744	80	38
Distillation, °C	ASTM D86		
IBP		162	176
10		200	198
20		212	208
30		224	220
40		236	234
50		248	249
60		259	260
70		271	271
80		284	281
90		299	291
FBP		316	305
Mass Spectrometry, wt% (Ref. 28)			
Saturates		59.52	69.09
Aromatics		40.48	30.91
Cetane Number	ASTM D619	31.2	36.9

TABLE 2.2

DISTILLATE ANALYSIS BY LOW-RESOLUTION MASS SPECTROMETRY

Hydrocarbon Type (CN.H2N-Z)	Z No	Syncrude Middle Distillate Mass Percent		Suncor Middle Distillate Mass Percent	
Saturates			59.60		69.09
Paraffins	+2	15.89		22.06	
Cycloparaffins			43.71		47.03
Noncond Cycloparaffins	0	21.12		24.00	
Cond Dicycloparaffins	-2	16.87		17.10	
Cond Polycycloparaffins	-4	5.72		5.92	
Aromatics			40.40		30.91
Monoaromatics			37.10		27.88
Alkylbenzenes	-6	19.45		14.06	
Benzocycloparaffins	-8	12.82		9.40	
Benzodicycloparaffins	-10	4.84		4.42	
Diaromatics			2.92		2.28
Naphthalenes	-12	2.10		1.43	
Naphthocycloparaffins	-14	0.00		0.00	
Fluorenes	-16	0.82		0.85	
Triaromatics			0.37		0.56
Phenanthrenes/Anthracene	-18	0.33		0.45	
Phenanthrocycloparaffins	-20	0.04		0.10	
Tetraaromatics			0.00		0.09
Pyrenes/Benzofluorenes	-22	0.00		0.06	
Chrysenes/Benzanthracene	-24	0.00		0.03	
Aromatic Sulfur			0.01		0.10
Benzothiophenes	-10S	0.01		0.06	
Dibenzothiophenes	-16S	0.00		0.04	
Benzonaphthothiophenes	-22S	0.00		0.00	

TABLE 2.3

SOLVENTS AND EXTRACTION TEMPERATURES USED IN THE PRELIMINARY EVALUATIONS

Solvent	Temperatures of Extraction, °C
Acetonitrile	20, 40, 60
Dimethyl Formamide	20, 40, 60
Nitroethane	10, 20, 25
Acetonitrile with 25% carbon disulphide	20
Acetonitrile with 10% carbon disulphide	20, 40
Acetone with 3% water	20
Acetone with 5% water	20
Acetone with 10% water	20
Methanol	20, 40, 60
Sulfolane	30, 50, 70
Dimethyl Sulphoxide	20, 40, 60
1-Methyl-2-pyrrolidone	10, 20, 25
N-Formylmorpholine	25
Tetraethylene Glycol	60
Furfural	20, 40, 70

TABLE 3.1

SOLVENTS EVALUATED FOR MIDDLE DISTILLATE EXTRACTION

Name	Formula	Density g/mL	Boiling Point, °C
Acetone (with water)	CH_3COCH_3	0.80	56
Methanol	CH_3OH	0.79	65
Furfural	C_5H_4O2	1.16	162
Acetonitrile (with and without carbon disulphide)	CH_3CN	0.78	82
Dimethyl Formamide (DMF)	$HCON(CH_3)_2$	0.94	153
Dimethylsulphoxide	$(CH_3)_2$ SO	1.10	189
Tetraethylene Glycol	$HOCH_2CH_2(OCH_2CH_2)_3OH$	1.13	327
Nitroethane	$C_2H_5NO_2$	1.05	114
Sulfolane	$CH_2CH_2CH_2CH_2SO_2$	1.26	285
1-Methyl-2-pyrrolidone	$CH_3N(CH_2)_3CO$	1.02	202
N-Formylmorpholine	$C_5H_9O_2N$	1.15	236
Sulphur Dioxide	SO_2	1.43	-10

TABLE 4.1

Evaluation of Solvents, Using Distribution Coefficients, Selectivity, Solvent and Refining Power. Syncrude Middle Distillate Feed

Solvent	Temp °C	Mass Balance % Feed	Arom.	K_a	K_s	$S_{a/s}$	X_2	Y	Z
Acetonitrile	20	99	94	0.26	0.02	12.2	0.51	0.10	0.056
density = 0.8081	40	108	108	0.46	0.08	5.8	0.38	0.22	0.084
bp = 82°C	60	102	102	0.48	0.08	6.3	0.43	0.23	0.099
				Good selectivity					
				Good solvent power					
				Adequate disengagement					
				Easy to distill away solvent					
Dimethyl Formamide	20	90	87	0.35	0.03	12.0	0.59	0.14	0.083
density = 0.9636	40	87	87	0.47	0.08	6.2	0.48	0.21	0.101
bp = 153°C	60	87	86	0.65	0.28	2.5	0.38	0.43	0.163
				Good selectivity					
				Good solvent power					
				Adequate disengagement					
Nitroethane	10	103.1	94.8	0.68	0.13	5.23	0.39	0.28	0.10
density = 1.0615	20	102.2	94.3	0.73	0.20	3.65	0.31	0.40	0.12
bp = 114°C	25	104.4	95.4	0.77	0.29	2.66	0.30	0.44	0.10
				Excellent solvent power					
				Poor selectivity					
				Refining power at par with acetonitrile, DMF					
Acetonitrile/CS_2									
25% CS_2	20	99.9	97.7	0.32	0.03	10.7	0.49	0.076	0.026
10% CS_2	20	99.4	96.7	0.25	0.02	11.8	0.52	0.082	0.049
10% CS_2	40	99.7	97.3	0.32	0.04	8.11	0.47	0.114	0.055
Acetonitrile:				Both selectivity and solvent power were decreased by the addition of CS_2 to acetonitrile.					
density = 0.8081									
bp = 82°C									
Carbon Disulfide:									
density = 1.260									
bp = 46°C									

TABLE 4.1 (continued)

Solvent	Temp °C	Mass Balance % Feed	Arom.	K_a	K_s	$S_{a/s}$	X_2	Y	Z
Acetone 3% H_2O	20	90.3	97.6	0.720	0.465	1.55	0.186	0.433	0.081
Acetone 5%H_2O	20	103.3	108.8	0.517	0.202	2.546	0.246	0.190	0.047
Acetone 10% H_2O	20	105.0	106.2	0.262	0.058	4.52	0.343	0.078	0.027
Acetone: density = 0.7997 bp = 56°C				Excellent solvent power (without water, acetone and middle distillate are miscible) Poor selectivity Poor disengagement					
Methanol	20	99	98	0.20	0.06	3.3	0.29	0.12	0.041
density = 0.7960	40	98	100	0.22	0.08	2.9	0.28	0.15	0.029
bp = 65°C	60	101	95	0.34	0.15	2.3	0.19	0.24	0.055
				Poor selectivity					
Sulfolane									
density = 1.2606(30/4)	30	100	95	0.091	0.006	15.6	0.52	0.04	0.02
bp = 285°C	50	100	96	0.103	0.008	12.4	0.50	0.04	0.02
mP = 28.5°C	70	102	97	0.211	0.026	8.2	0.44	0.06	0.02
				Good selectivity Poor solvent power					
Dimethyl Sulphoxide	20	96	91	0.03	0	--	0.63	0.01	0.02
density = 0.1101	40	94	83	0.04	0.002	17	6.53	0.02	0.06
bp = 189°C	60	91	87	0.05	0.001	46	0.62	0.02	0.06
Decomposes to SO_x at 189°C				Good selectivity Poor solvent power					

TABLE 4.1 (continued)

Solvent	Temp °C	Mass Balance % Feed	Arom.	K_a	K_s	$S_{a/s}$	X_2	Y	Z
N-Methyl-Pyrrolidone	10	71	60	0.97	0.09	10.0	0.61	0.34	0.13
density = 1.0386	20	72	57	0.70	0.30	2.3	0.15	0.46	0.10
bp = 202°C	25	68	80	0.69	0.51	1.4	0.37	6.27	0.08
				Good solvent power					
				Fair selectivity					
				Difficult to separate extract from solvent					
N-Formylmorpholin	25	100 (calculated)	100	0.144	--	unde-fined	0.052	0.035	
density = 1.1603									
bp = 285°C									
				Good selectivity					
				Poor solvent power					
				Difficult to separate					
Tetraethylene glycol	60	98.6	99.6	0.051	0.0052	9.8	0.49	0.022	0.011
density = 1.1323				Poor solvent power					
bp = 327°C									
Furfural	20	90.6	85.7	0.208	0.024	8.67	0.516	0.087	0.054
density = 1.1635	40	94.4	91.1	0.356	0.093	3.83	0.350	0.176	0.057
bp = 162°C	70	88.2	85.8	0.571	0.205	2.79	0.354	0.302	0.059
				Good solvent power					
				Fair selectivity					
				Difficult to separate extract from solvent					
Sulphur Dioxide*	-12	N.D.	N.D.	0.56	0.03	18.7	N.D.	N.D.	N.D.
density = 1.43	2	N.D.	N.D.	0.62	0.08	7.8	N.D.	N.D.	N.D.
bp = -10°C	17	N.D.	N.D.	0.78	0.26	3.0	N.D.	N.D.	N.D.

*Section 4.3; some of the data are given here for comparison

N.D. = Not Determined

TABLE 4.2

Tie-Line Data from SO_2 Extractions of Syncrude Middle Distillate

Experiment Number	Temp. °C	Nominal Solvent/Oil Ratio vol/vol	Actual Solvent/Oil Ratio wt/wt	Hydrocarbon Content of the Extract Phase wt.%	Hydrocarbon Content of the Raffinate Phase wt.%	Aromatics Content of the Extract wt.%	Aromatics Content of the Raffinate wt.%
3	1.5	0.50:1	0.9038	24.33	63.75	74.39	35.13
4	2.9	1.00:1	1.5973	17.12	72.38	73.53	27.73
7	2.2	2.00:1	3.7101	10.78	79.14	73.58	18.85
8	0.6	1.00:1	1.6772	17.08	76.48	74.81	27.15
9	-12.2	1.00:1	1.7790	14.02	82.82	86.95	26.25
10	-11.8	0.50:1	0.8051	23.02	79.22	82.84	33.58
12	-12.0	1.25:1	2.0675	11.33	82.21	87.44	24.28
13	-11.5	1.50:1	2.3957	11.99	83.25	87.26	23.28
16	2.0	1.25:1	2.0592	16.05	76.97	73.83	25.29
17	17.5	1.00:1	1.5832	25.43	61.21	56.67	30.29
20	16.8	1.25:1	2.0217	20.39	67.66	59.45	26.46
21	17.5	1.50:1	2.5419	17.87	71.16	57.72	23.42

Feed aromatics content: 40.44 wt.%.

TABLE 4.2 (continued)

Experiment Number	Temp. °C	Nominal Solvent/Oil Ratio vol/vol	Actual Solvent/Oil Ratio wt/wt	Hydrocarbon Content of the "Extract" Phase wt.%	Hydrocarbon Content of the "Raffinate" Phase wt.%	Aromatics Content of the "Extract" wt.%	Aromatics Content of the "Raffinate" wt.%
5*	2.4	0.25:1	0.4421	71.2	70.7	39.54	39.27
11*	-12.0	0.25:1	0.4282	72.3	72.3	39.71	39.15
18*	17.3	0.50:1	0.8617	54.5	54.2	40.37	40.36
19*	17.4	0.25:1	0.4399	70.3	72.1	41.06	40.98

* These experiments yielded single phase mixtures and were not used in further studies.

TABLE 4.3

Tie-Line Data from SO_2 Extractions of Suncor Middle Distillate

Experiment Number	Temp. °C	Nominal Solvent/Oil Ratio vol/vol	Actual Solvent/Oil Ratio wt/wt	Hydrocarbon Content of the Extract Phase wt.%	Hydrocarbon Content of the Raffinate Phase wt.%	Aromatics Content of the Extract wt.%	Aromatics Content of the Raffinate wt.%
23	17.5	0.50:1	0.84	38.33	63.45	43.06	28.69
24	17.5	0.75:1	1.29	19.80	67.15	54.52	23.69
25	17.5	1.00:1	1.76	17.67	69.63	53.22	20.91
27	17.5	1.50:1	2.48	15.06	72.49	52.89	17.67
28	17.5	2:00:1	3.34	12.26	73.22	52.70	15.31
29	2.5	0.50:1	0.91	16.73	76.17	71.83	24.75
30	2.5	0.75:1	1.29	13.54	78.00	72.29	21.82
31	2.5	1.00:1	1.66	12.64	80.05	72.36	20.05
33	2.5	1.50:1	2.50	10.32	82.18	68.97	17.02
35	-12.0	0.50:1	0.89	13.93	82.26	85.48	23.82
36	-12.0	0.75:1	1.26	12.36	82.93	84.45	22.04
37	-12.0	1.00:1	1.76	10.43	84.89	83.62	19.57
38	-12.0	1.25:1	2.00	9.82	83.57	83.07	18.89
39	-12.0	1.75:1	3.06	8.03	85.69	81.02	16.25

Feed aromatics content: 30.88 wt.%

TABLE 4.4

Acetonitrile Extractions of Syncrude Middle Distillate
Raw Experimental Data

Experiment Number	Temp. °C	Nominal Solvent/Oil Ratio vol/vol	Feed g	Solvent g	Raffinate Phase g	Raffinate Phase Density g/mL	Solvent Content of the Raffinate Phase vol.%	Aromatics Content of the Raffinate Hydrocarbons wt.%
Syncrude								
16	0	1.0	176.5	155.0	162.8	0.8548	1.85	35.91
17	0	0.5	257.9	117.4	249.9	0.8561	1.95	37.66
18	0	0.6	258.0	141.8	247.1	0.8559	1.81	37.29
19	0	0.7	213.9	136.1	203.9	0.8556	1.68	36.85
20	0	0.8	218.5	156.2	205.9	0.8554	1.78	36.44
21	0	1.25	173.7	194.8	157.5	0.8542	1.80	34.89
105	0	10	43.0	398.1	23.0	0.8441	1.30	19.49
106	0	7	59.3	382.0	37.3	0.8464	1.13	22.71
107	0	4	84.9	312.8	63.3	0.8496	1.30	26.90
108	0	2	170.0	297.5	146.2	0.8529	1.51	31.82
3	12	0.5	250.7	112.6	241.6	0.8558	2.60	36.95
4	12	0.7	214.5	136.5	202.9	0.8548	2.39	35.62
5	12	1.25	170.7	194.6	153.5	0.8531	2.23	34.03
8	12	2	133.3	230.7	112.9	0.8520	2.20	31.91
24	11	1	173.2	157.6	156.6	0.8536	2.18	34.85
9	20	0.5	260.2	116.8	251.1	0.8551	2.82	36.70
10	20	0.6	256.0	140.9	244.6	0.8547	2.80	36.20
11	20	0.7	212.7	135.7	200.6	0.8543	2.82	35.58
12	20	0.8	216.7	155.4	202.6	0.8540	2.71	35.49
13	20	1	174.0	157.5	158.3	0.8534	2.60	34.59
22	20	1.25	175.8	197.4	156.7	0.8527	3.00	33.35
23	20	2	130.2	250.9	105.2	0.8507	2.39	30.67
100	20	10	35.5	320.4	15.5	0.8431	1.34	17.60
101	20	7	43.6	272.5	24.3	0.8445	1.87	21.35
102	20	5	68.1	314.5	42.0	0.8465	1.88	24.16
103	20	1.7	169.0	266.0	141.7	0.8520	2.35	31.61
213	30	1	172.1	158.8	154.0	0.8533	2.42	33.94
214	30	2	131.3	252.7	104.8	0.8506	2.06	29.13
215	30	4	87.2	314.2	56.4	0.8474	1.73	25.67
216	30	6	63.4	354.8	35.0	0.8448	1.66	21.82
217	30	10	44.0	391.4	18.2	0.8424	1.98	17.59

TABLE 4.5

Acetonitrile Extractions of Suncor Middle Distillate
Raw Experimental Data

Experiment Number	Temp. °C	Nominal Solvent/Oil Ratio vol/vol	Feed g	Solvent g	Raffinate Phase g	Raffinate Phase Density g/mL	Solvent Content of the Raffinate Phase vol.%	Aromatics Content of the Raffinate Hydrocarbons wt.%
38	0	0.6	255.2	142.5	246.8	0.8459	1.33	28.22
40	0	0.8	215.7	157.7	205.4	0.8456	1.16	27.78
41	0	1	171.2	158.1	160.1	0.8449	1.27	27.06
42	0	1.25	169.9	195.9	156.2	0.8443	1.18	26.28
205	0	2	168.3	314.8	147.8	0.8436	1.43	24.66
206	0	6	78.2	422	56.3	0.8387	1.2	18.47
32	10	0.6	256.7	141.5	248.3	0.8452	1.56	27.56
34	10	0.8	214.4	156.2	204	0.8447	1.6	26.54
35	10	1	171.9	159.7	160.7	0.8441	1.6	25.67
36	10	1.25	173.4	197.1	158.9	0.8436	1.52	25.05
203	10	2	169	310	147.5	0.8429	1.69	23.55
204	10	6	83.7	470.1	57.2	0.8376	2.16	18.26
26	20	0.6	253.4	141.2	244.3	0.8445	2.1	27.29
28	20	0.8	212.6	155.9	201.4	0.844	1.92	26.33
29	20	1	172.1	156.2	159.4	0.8433	2.03	25.2
30	20	1.25	173.2	194.6	157.9	0.8427	1.92	24.53
201	20	2	210.1	387.1	181	0.8427	1.98	23.73
202	20	6	84	466.7	55.4	0.8376	1.62	16.97
207	20	10	41	392.7	21.4	0.835	1.42	13.19

TABLE 4.6

Dimethyl Formamide Extractions of Syncrude Middle Distillate
Raw Experimental Data

Experiment Number	Temp. °C	Nominal Solvent/Oil Ratio vol/vol	Feed g	Solvent g	Raffinate Phase g	Raffinate Phase Density g/mL	Solvent Content of the Raffinate Phase vol.%	Aromatics Content of the Raffinate Hydrocarbons wt.%
9	0	1.0	174.8	191.6	146.1	0.8547	3.22	30.02
10	0	0.5	255.8	143.4	236.4	0.8585	3.62	33.51
11	0	0.6	257.1	170.9	232.3	0.8578	3.37	32.74
12	0	0.7	218.5	165.2	193.6	0.8571	3.54	32.32
14	0	1.25	171.8	236.8	137.6	0.8531	3.02	28.51
15	0	1.5	132.6	301.1	95.0	0.8500	3.08	24.64
2	10	1.0	172.4	188.8	141.2	0.8551	4.10	28.94
3	10	0.5	258.4	142.3	238.4	0.8593	4.70	32.64
4	10	0.6	258.8	171.0	232.5	0.8583	4.61	31.88
5	10	0.7	214.1	165.4	187.5	0.8573	4.57	32.32
6	10	0.8	215.6	189.3	184.5	0.8565	4.40	30.44
7	10	1.25	171.1	236.6	133.4	0.8537	4.32	27.44
8	10	2.0	128.0	301.2	85.3	0.8494	3.76	23.27
16	20	0.5	260.0	143.3	240.8	0.8600	5.85	32.59
17	20	0.6	260.8	170.9	233.1	0.8601	5.98	31.55
18	20	0.7	216.1	165.7	186.9	0.8590	5.75	30.88
19	20	0.8	214.9	190.3	179.9	0.8579	5.44	29.96
20	20	1.0	175.7	190.4	140.0	0.8565	5.00	28.63
21	20	1.25	173.0	239.2	128.9	0.8547	4.82	26.86
210	20	2.0	169.7	377.8	105.7	0.8505	4.06	23.76
211	20	6.0	84.7	577.8	23.5	0.8398	2.98	12.93

TABLE 4.7

Dimethyl Formamide Extractions of Suncor Middle Distillate
Raw Experimental Data

Experiment Number	Temp. °C	Nominal Solvent/Oil Ratio vol/vol	Feed g	Solvent g	Raffinate Phase g	Raffinate Phase Density g/mL	Solvent Content of the Raffinate Phase vol.%	Aromatics Content of the Raffinate Hydrocarbons wt.%
35	0	0.6	255.4	171.4	238.1	0.8469	2.82	24.87
37	0	0.8	212.0	190.6	191.4	0.8455	2.61	23.68
38	0	1.0	170.3	191.9	149.2	0.8443	2.53	22.53
39	0	1.25	171.9	236.5	146.6	0.8432	2.47	21.37
28	10	0.5	254.0	142.4	240.6	0.8483	3.65	24.88
29	10	0.6	253.4	172.4	235.2	0.8477	3.63	24.06
30	10	0.7	210.0	164.2	191.4	0.8467	3.39	23.64
32	10	1.0	172.0	190.4	149.0	0.8451	3.36	21.93
33	10	1.25	174.9	238.3	146.5	0.8440	3.37	20.79
22	20	0.5	255.4	142.1	242.7	0.8499	4.14	24.43
23	20	0.6	255.8	172.1	236.3	0.8486	4.22	24.01
24	20	0.7	210.5	166.0	190.2	0.8481	4.28	23.2
25	20	0.8	214.3	189.2	190.4	0.8473	4.22	22.84
26	20	1.0	175.0	191.0	149.4	0.8459	3.94	21.88
27	20	1.25	170.8	237.2	139.1	0.8444	3.85	20.31
208	20	2	169.8	380.6	121.0	0.8417	3.42	17.87
209	20	6	85.1	572.8	34.0	0.8335	2.54	11.13

TABLE 4.8

Nitrogen Contents of Raffinates and Extracts from Single-Stage SO_2 Extractions of Syncrude Middle Distillate

Experiment Number	Temp. °C	Nominal Solvent/Oil Ratio vol/vol	Nitrogen Content, ppm by wt	
			Raffinate	Extract
3	1.5	0.50:1	14.5	132
7	2.2	2.00:1	1.6	53.6
10	-11.8	0.50:1	6.5	158
13	-11.5	1.50:1	1.7	100
17	17.5	1.00:1	16.2	72.7
21	17.5	1.50:1	3.5	53.3

TABLE 4.9

Sulphur Contents of Raffinates from Single-Stage Acetonitrile Extractions of Syncrude Middle Distillate

Temp. °C	Experiment Number	Nominal Solvent/Oil Ratio vol/vol	Raffinate Sulphur Content ppm by wt
0	17	0.5	160
0	21	1.25	145
0	105	10	72
12	3	0.5	162
12	8	2	132
20	9	0.5	156
20	23	2	120
20	100	10	64
30	214	2	100
30	217	10	50

TABLE 4.10

Sulphur Contents of Raffinates from Single-Stage Dimethyl Formamide Extractions of Syncrude Middle Distillate

Temp. °C	Experiment Number	Nominal Solvent/Oil Ratio vol/vol	Raffinate Sulphur Content ppm by wt
0	10	0.5	110
0	15	1.5	60
10	3	0.5	110
10	8	2.0	60
20	16	0.5	110
20	21	1.25	75
20	210	2.0	50
20	211	6.0	30

TABLE 4.11

Subgroup Selectivity Study -
Syncrude and Suncor Middle Distillate Analyses

	Syncrude	Suncor
Paraffins, wt.%	15.39	22.21
Non-Condensed Cycloparaffins, wt.%	21.48	23.70
Condensed Cycloparaffins, wt.%	22.69	23.21
Alkylbenzenes, wt.%	19.59	13.98
Balance (mostly condensed aromatics) wt.%	20.85	16.90
	100.00	100.00

TABLE 4.12

Subgroup Selectivity Study
Data from SO_2 Extractions of Syncrude and Suncor Middle Distillates

Experiment No.	Feed Type	Temp. °C	Nominal Solvent/Oil Ratio vol/vol	Actual Solvent/Oil Ratio wt/wt	Hydrocarbon Content of the Extract Phase wt.%	Hydrocarbon Content of the Raffinate Phase wt.%	Analyses of the Extract Hydrocarbons				Analyses of the Raffinate Hydrocarbons			
							Paraffins wt.%	Non-Condensed Cyclo-paraffins wt.%	Condensed Cyclo-paraffins wt.%	Alkyl-benzenes wt.%	Paraffins wt.%	Non-Condensed Cyclo-paraffins wt.%	Condensed Cyclo-paraffins wt.%	Alkyl-benzenes wt.%
9	Syncrude	-12.2	1.00	1.7790	14.02	82.82	2.19	5.41	5.37	39.19	19.14	26.74	27.87	12.69
10	"	-11.8	0.50	0.8051	23.02	79.22	2.80	7.84	6.50	38.55	17.17	24.17	25.08	16.17
12	"	-12.0	1.25	2.0675	11.33	82.21	2.04	5.34	5.10	39.59	20.62	26.81	28.29	11.89
13	"	-11.5	1.50	2.3957	11.99	83.25	2.47	5.43	4.84	39.56	20.71	26.63	29.38	11.39
35	Suncor	-12.0	0.50	0.89	13.93	82.26	3.44	6.06	5.02	37.70	24.29	25.49	26.40	11.04
36	"	-12.0	0.75	1.26	12.36	82.93	3.65	6.79	5.11	37.11	25.22	25.19	27.55	10.19
37	"	-12.0	1.00	1.76	10.43	84.89	4.12	6.91	5.35	36.65	25.73	26.89	27.81	9.12
38	"	-12.0	1.25	2.00	9.82	83.57	4.03	7.29	5.61	36.61	25.73	26.90	28.48	8.73
39	"	-12.0	1.75	3.06	8.03	85.69	4.44	8.23	6.31	35.37	26.62	26.94	30.19	7.30

TABLE 4.13

Subgroup Selectivity Study - Data from Single-Stage
Acetonitrile Extractions of Syncrude and Suncor Middle Distillates

Experiment Number	Feed Type	Temp. °C	Nominal Solvent/Oil Ratio vol/vol	Feed g	Solvent g	Raffinate Phase g	Raffinate Phase Density g/mL	Solvent Content of the Raffinate Phase vol.%	Analyses of the Raffinate Hydrocarbons			
									Paraffins wt.%	Non-Condensed Cycloparaffins wt.%	Condensed Cycloparaffins wt.%	Alkylbenzenes wt.%
11	Syncrude	20	0.7	212.7	135.7	200.6	0.8543	2.02	17.20	22.96	24.26	16.86
12	"	20	0.8	216.7	155.4	202.6	0.8540	2.71	17.00	23.41	24.10	16.62
13	"	20	1	174.0	157.5	150.3	0.8534	2.60	17.00	24.07	24.26	16.13
22	"	20	1.25	175.8	197.4	156.7	0.8527	3.08	17.00	23.84	25.01	15 20
23	"	20	2	130.2	250.9	105.2	0.8507	2.39	18.50	24.95	25.00	13.96
100	"	20	10	35.5	320.4	15.5	0.8431	1.34	23.53	28.24	30.63	7.62
101	"	20	7	41.6	272.5	24.3	0.8445	1.07	22.01	27.41	29.23	9.05
102	"	20	5	68.1	314.5	42.8	0.8465	1.08	20.02	26.03	28.19	10.36
103	"	20	1.7	169.0	266.0	141.7	0.8520	2.35	18.27	24.56	25.56	14.64
26	Suncor	20	0.6	253.4	141.2	244.3	0.8445	2.1	23.91	26.61	24.19	12.16
28	"	20	0.8	212.6	155.9	201.4	0.844	1.92	24.39	24.91	24.37	11.98
29	"	20	1	172.1	156.2	159.4	0.8433	2.03	24.46	25.35	24.99	11.40
30	"	20	1.25	173.2	194.6	157.9	0.8427	1.92	25.01	25.44	25.02	11.06
201	"	20	2	210.1	387.1	181	0.8427	1.98	24.47	25.44	26.36	9.96
202	"	20	6	84	466.7	55.4	0.8376	1.62	27.14	26.87	29.02	6.74
207	"	20	10	41	392.7	21.4	0.835	1.42	29.37	27.77	29.67	5.28

TABLE 4.14

Subgroup Selectivity Study - Data from
Dimethyl Formamide Extractions of Syncrude and Suncor Middle Distillates

Experiment Number	Feed Type	Temp. °C	Nominal Solvent/Oil Ratio vol/vol	Feed g	Solvent g	Raffinate Phase g	Raffinate Phase Density g/mL	Solvent Content of the Raffinate Phase vol.%	Analyses of the Raffinate Hydrocarbons			
									Paraffins wt.%	Non-Condensed Cycloparaffins wt.%	Condensed Cycloparaffins wt.%	Alkylbenzenes wt.%
16	Syncrude	20	0.5	260.0	143.3	240.0	0.8680	5.85	18.68	23.79	24.94	16.35
17	"	20	0.6	260.0	170.9	233.1	0.8681	5.90	19.19	23.83	25.43	15.73
18	"	20	0.7	216.1	165.7	186.9	0.8590	5.75	19.44	23.84	25.86	15.46
19	"	20	0.8	214.9	190.3	179.9	0.8579	5.44	19.93	24.20	25.91	14.94
20	"	20	1.0	175.7	198.4	140.0	0.8565	5.80	20.29	24.81	26.27	14.23
21	"	20	1.25	173.0	219.2	128.9	0.8547	6.02	20.85	25.38	26.99	13.19
210	"	20	2.0	169.7	377.8	105.7	0.8505	6.86	22.16	26.77	27.31	10.96
211	"	20	6.0	84.7	577.8	23.5	0.8398	2.90	27.44	29.75	29.88	5.98
35	Suncor	0	0.6	255.4	171.4	238.1	0.8469	2.82	24.64	24.98	25.51	11.54
37	"	0	0.8	212.8	190.6	191.4	0.8455	2.61	25.17	25.30	25.85	10.88
38	"	0	1.0	170.3	191.9	149.2	0.8443	2.53	25.76	24.74	26.97	10.35
39	"	0	1.25	171.9	236.5	146.6	0.8432	2.47	26.85	25.91	26.67	9.74

TABLE 4.15

Subgroup Selectivity Study -
Paraffin and Non-Condensed Cycloparaffin Contents
of Feed and Raffinate Saturates, Alkylbenzene Content
of Feed and Raffinate Aromatics.
Single-Stage SO_2 Extractions of Syncrude and Suncor Middle Distillates

Experiment Number	Type of Sample	Temp. °C	Nominal Solvent/Oil Ratio vol/vol	Paraffins in the Saturates, wt. fraction	Non-Condensed Cycloparaffins in the Saturates, wt. fraction	Alklybenzenes in the Aromatics, wt. fraction
-	Syncrude Feed	-	-	0.2584	0.3606	0.4844
9	Syncrude Raffinate	-12.2	1.00	0.2595	0.3626	0.4834
10	" "	-11.8	0.50	0.2585	0.3639	0.4815
12	" "	-12.0	1.25	0.2723	0.3541	0.4897
13	" "	-11.5	1.50	0.2699	0.3471	0.4893
-	Suncor Feed	-	-	0.3213	0.3429	0.4527
35	Suncor Raffinate	-12.0	0.50	0.3188	0.3346	0.4635
36	" "	-12.0	0.75	0.3235	0.3231	0.4623
37	" "	-12.0	1.00	0.3199	0.3343	0.4660
38	" "	-12.0	1.25	0.3172	0.3316	0.4621
39	" "	-12.0	1.75	0.3178	0.3217	0.4492

TABLE 4.16

Subgroup Selectivity Study -
Paraffin and Non-Condensed Cycloparaffin Contents
of Feed and Raffinate Saturates, Alkylbenzene Content
of Feed and Raffinate Aromatics.
Single-Stage Acetonitrile Extractions of Syncrude and Suncor Middle Distillates

Experiment Number	Type of Sample	Temp. °C	Nominal Solvent/Oil Ratio vol/vol	Paraffins in the Saturates, wt. fraction	Non-Condensed Cycloparaffins in the Saturates, wt. fraction	Alkylbenzenes in the Aromatics, wt. fraction
-	Syncrude Feed	-	-	0.2584	0.3606	0.4844
11	Syncrude Raffinate	20	0.7	0.2670	0.3564	0.4739
12	" "	20	0.8	0.2635	0.3629	0.4683
13	" "	20	1.0	0.2611	0.3680	0.4663
22	" "	20	1.25	0.2671	0.3577	0.4582
23	" "	20	2.0	0.2668	0.3599	0.4552
100	" "	20	10.0	0.2856	0.3427	0.4330
101	" "	20	7.0	0.2798	0.3485	0.4239
102	" "	20	5.0	0.2745	0.3538	0.4288
103	" "	20	1.7	0.2671	0.3591	0.4631
-	Suncor Feed	-	-	0.3213	0.3429	0.4527
26	Suncor Raffinate	20	0.6	0.3288	0.3385	0.4456
28	" "	20	0.8	0.3311	0.3381	0.4550
29	" "	20	1.0	0.3270	0.3389	0.4524
30	" "	20	1.25	0.3314	0.3371	0.4509
201	" "	20	2.0	0.3208	0.3336	0.4197
202	" "	20	6.0	0.3269	0.3236	0.3972
207	" "	20	10.0	0.3383	0.3199	0.4003

TABLE 4.17

Subgroup Selectivity Study -
Paraffin and Non-Condensed Cycloparaffin Contents
of Feed and Raffinate Saturates, Alkylbenzene Content
of Feed and Raffinate Aromatics.
Single-Stage Dimethyl Formamide Extractions of Syncrude and Suncor Middle Distillates

Experiment Number	Type of Sample	Temp. °C	Nominal Solvent/Oil Ratio vol/vol	Paraffins in the Saturates, wt. fraction	Non-Condensed Cycloparaffins in the Saturates, wt. fraction	Alklybenzenes in the Aromatics, wt. fraction
-	Syncrude Feed	-	-	0.2584	0.3606	0.4844
16	Syncrude Raffinate	20	0.5	0.2771	0.3529	0.5017
17	" "	20	0.6	0.2804	0.3481	0.4986
18	" "	20	0.7	0.2812	0.3449	0.5006
19	" "	20	0.8	0.2846	0.3455	0.4987
20	" "	20	1.0	0.2843	0.3476	0.4970
21	" "	20	1.25	0.2851	0.3459	0.4911
210	" "	20	2.0	0.2907	0.3511	0.4604
211	" "	20	6.0	0.3151	0.3417	0.4625
-	Suncor Feed	-	-	0.3213	0.3429	0.4527
35	Suncor Raffinate	0	0.6	0.3280	0.3325	0.4640
37	" "	0	0.8	0.3298	0.3315	0.4595
38	" "	0	1.0	0.3325	0.3193	0.4594
39	" "	0	1.25	0.3313	0.3295	0.4558

TABLE 4.18

Comparison of Measured and Calculated Cetane Numbers

Sample	Cetane Number		Aromatics Content wt.%
	Measured*	Calculated**	
Product Blend A	43.9	41.5	24.03
Product Blend B	40.6	38.6	26.52
Product Blend C	45.0	42.0	22.27

* ASTM D-613

** New, "general-purpose" Petro-Canada Products R&D Centre correlation

TABLE 4.19

Thermodynamic Simulation of Tie-Line Data
Observed and Calculated Major Trends on a Large
Increase of the Solvent/Oil Ratio - Single-Stage
Acetonitrile Extractions of Syncrude Middle Distillate

Experiment Number	Solvent/Oil Ratio wt/wt	Saturates/Aromatics Ratio in the Raffinate, wt/wt		Aromatics/Saturates Ratio in the Extract, wt/wt	
		Experimental	Calculated	Experimental	Calculated
11	0.6380	1.81	1.82	20.25	16.44
23	1.927	2.26	2.89	3.39	14.14
100	9.025	4.68	9.32	1.367	6.956

TABLE 4.20

Batch Simulation (29) of Three-Stage Continuous Extraction with Acetonitrile at 20°C, Syncrude Middle Distillate Feed

Density of the Raffinates and Extracts - Approach to Steady State

Raffinate Phases	Extract Phases
No. 1 = 0.8424 g/cc	No. 1 = 0.7957 g/cc
No. 2 = 0.8443 g/cc	No. 2 = 0.7974 g/cc
No. 3 = 0.8458 g/cc	No. 3 = 0.7981 g/cc
No. 4 = 0.8464 g/cc	No. 4 = 0.7992 g/cc
No. 5 = 0.8467 g/cc	No. 5 = 0.7991 g/cc

Compositions of the Final Streams

	Raffinate Phase No. 5 (wt.%)	Extract Phase No. 6 (wt.%)
Aromatics	23.0	12.6
Non-aromatics	75.0	1.7
Solvent	2.0	85.7

TABLE 4.21

Acetonitrile Extractions of Syncrude and Suncor Middle Distillates
Pilot Plant Survey Run Experimental Data

Experiment Number	Temp. °C	Nominal Solvent/Oil Ratio vol/vol	Actual Solvent/Oil Ratio wt/wt	Nominal Feed Rate mL/h	Actual Feed Rate mL/h	Feed g	Solvent g	Raffinate Phase g	Raffinate Phase Density g/mL	Solvent Content of the Raffinate Phase vol.%	Aromatics Content of the Raffinate Hydrocarbons wt.%
Syncrude											
20-4	20	2.0	1.98	300	300	258.6	511.6	202.3	0.8488	1.1	26.07
20-9	20	1.5	1.48	300	300	258.6	381.7	212.6	0.8507	1.0	28.06
20-23	20	3.0	3.30	200	180	155.2	511.6	86.6	0.8420	2.0	17.89
20-12	30	2.0	1.92	200	215	366.4	684.7	275.6	0.8469	1.9	23.12
20-14	30	2.5	2.47	200	200	172.4	425.0	111.2	0.8456	1.6	20.37
Suncor											
20-17	20	1.6	1.62	200	200	672.4	1086.1	581.6	0.8413	0.9	20.41
20-19	20	1.6	1.50	200	200	515.0	779.1	432.0	0.8414	0.9	19.15
20-22	20	1.6	1.57	300	300	255.4	401.4	215.9	0.8414	1.1	21.66

TABLE 4.22

Characterization of Raffinates from Pilot Plant Survey Runs*

Tests	Test Method	Run #1	Run #2	Run #3	Run #4	Run #7	Run #9	Run #10	Run #12	Run #13	Run #14	Run #15	Run #17	Run #20	Run #22
Acetonitrile, vol.%	Gas Chromatography	0.82	0.80	1.37	1.05	0.20	0.96	0.55	2.46	0.30	0.19	0.23	0.91	0.61	1.13
Density @ 15C, g/cc	ASTM D4052	0.8482	0.8508	0.8501	0.8501	0.8598	0.8512	0.8501	0.8472	0.8491	0.8458	0.8447	0.8425	0.8425	0.8436
Viscosity @ 40C, cSt	ASTM D445		2.39	2.44	2.41		2.36	2.48	2.46		2.53		2.35	2.34	2.33
Cloud Point, °C	ASTM D2500		-45	-39	-45	-39	-45	-43	-40		-42		-38	-33	-38
Pour Point, °C	ASTM D97		-63	<-51	-57	-57	-60	-60	<-51		-51		-51	<-51	<-51
Flash Point, °C	ASTM D56			58	65	69	55							73	73
Aniline Point, °C	ASTM D611	59.6	55.9	56.1	56.5	59.6	52.9	56.4	59.6	56.6	60.5	62.6	61.3	61.6	60.9
H_2O, ppm by wt.	ASTM D1774	232	77	63	96	128	57	59	47	65	60	66		22	39
Total N, ppm by wt.	ASTM D3431	268	37	66	84	16	175	112	39	38	23	30	23.5	21.6	85.6
Total S, ppm by wt.	ASTM D1552	140	170	170	150	140	180	170	140	140	120	100	400	400	410
Distillation, D86	ASTM D86														
IBP, °C			175					170	173	175		179	190		190
10			204					207	206	205		208	210		210
20			219					220	220	220		222	220		220
30			230					231	233	232		234	232		231
40			242					243	244	243		245	243		243
50			253					254	255	254		256	254		254
60			264					264	266	265		267	264		264
70			275					275	277	275		277	273		272
80			281					287	288	287		284	282		282
90			300					301	301	300		302	292		191
FBP			317					316	317	317		317	304		303
Cetane Index, ASTM	ASTM D976		43.7					44.2	45.3	44.5		46.4	46.7		46.3

*Of the experiments listed in Tables 4.21 and V.1, some did not provide sufficient raffinate to carry out the above characterization studies.

TABLE 4.23

Inspections of the "Production Run" Composite Raffinate

		Test Method	
Density at 15°C, g/cc		ASTM D4052	0.8513
Distillation D86	IBP, °C	ASTM D86	200
	10		216
	20		227
	30		238
	40		248
	50		259
	60		269
	70		279
	80		290
	90		308
	FBP		322
Flash Point, °C		ASTM D56	69
Cloud Point, °C		ASTM D2500	-43
Pour Point, °C		ASTM D97	<-63
Aniline Point, °C		ASTM D611	58.7
Viscosity at 40°C, cSt		ASTM D445	2.53
Total N ppm by wt		ASTM D3431	66.3
Total S ppm by wt		ASTM D1552	131.4
Cetane Index (ASTM)		ASTM D976	45.0
Cetane Number		ASTM D613	42.2
Water (Karl Fischer) ppm by wt		ASTM D1774	57

TABLE 4.24

Inspections of Jet A-Type Fuel Fraction of "Production Run" Syncrude Raffinate

		Test Method	
Density at 15°C, g/cc		ASTM D4052	0.8450
Distillation D86	IBP, °C	ASTM D86	190
	10		212
	20		219
	30		229
	40		237
	50		245
	60		254
	70		263
	80		272
	90		286
	FBP		300
Cloud Point, °C		ASTM D2500	-46
Pour Point, °C		ASTM D97	-60
Freeze Point, °C		ASTM D2386	-46
Aniline Point, °C		ASTM D611	58.3
Smoke Point		ASTM D1322	18.4
Copper Corrosion		ASTM D130	1a
Viscosity at -20C, cSt		ASTM D445	10.59

Table 4.25

Subgroup Selectivity Study -
Paraffin and Non-Condensed Cycloparaffin Contents of Feed and
Raffinate Saturates, Alkylbenzene Content of Feed and Raffinate Aromatics.
Pilot Plant Acetonitrile Extractions of Syncrude and Suncor Middle Distillates at 20°C

Experiment Number	Type of Sample	Temp. °C	Nominal Solvent/Oil Ratio wt/wt	Paraffins in the Saturates, wt. fraction	Non-Condensed Cycloparaffins in the Saturates, wt. fraction	Alklybenzenes in the Aromatics, wt. fraction
-	Syncrude Feed	-	-	0.2584	0.3606	0.4844
20-4	Syncrude Raffinate	20	2.0	0.2774	0.3494	0.4074
20-9	" "	20	1.5	0.2754	0.3497	0.4316
-	Suncor Feed	-	-	0.3213	0.3429	0.4527
20-17	Suncor Raffinate	20	1.6	0.3223	0.3279	0.3915
20-19	" "	20	1.6	0.3228	0.3297	0.3953
20-22	" "	20	1.6	0.3282	0.3213	0.3924

TABLE 4.26

Actual and Recalculated (Subgroup Selectivity Effects Cancelled) Compositions of Syncrude Raffinate from Pilot Plant Experiment No. 20-9 (Acetonitrile Extraction at 20°C)

Hydrocarbon Type	wt.% in Raffinate	wt.% in Recalculated* Raffinate
Paraffins	19.81	18.589
Non-Condensed Cycloparaffins	25.16	25.939
Condensed Dicycloparaffins	19.70	20.823
Condensed Polycycloparaffins	7.27	6.589
Alkylbenzenes	12.11	13.593
Benzocycloparaffins and Benzodicycloparaffins	14.03	12.278
Naphthalenes	0.87	1.433
Balance ("Other" Aromatics)	1.05	0.756
Corresponding Cetane Number Prediction:	38.3	36.4

Relative Concentrations, wt. fraction	Raffinate	Feed
Paraffins/Saturates	0.2754	0.2584
Non-Cond. Cyclopar./Saturates	0.3497	0.3606
Cond. Dicyclopar./Saturates	0.2738	0.2894
Cond. Polycyclopar./Saturates	0.1011	0.0916
Alkylbenzenes/Aromatics	0.4316	0.4844
Benzocyclo- and Benzodicyclopar./Aromatics	0.5000	0.4376
Naphthalenes/Aromatics	0.0310	0.0511
Balance/Aromatics	0.0374	0.0269

*Total saturates and aromatics as in "real" raffinate, relative subgroup concentrations as in feed.

TABLE 4.27

The Influence of Subgroup Selectivity on Raffinate Quality. Estimated Cetane Numbers of Syncrude and Suncor Raffinates - and of the Hypothetical Raffinates that One Would Obtain in the Absence of Subgroup Fractionation

Experiment or Sample Number	Type of Sample	Solvent	Temp. °C	Nominal Solvent/Oil Ratio vol/vol	Number of Theoretical Stages	Cetane Number Estimate From Actual Raffinate Composition	Cetane Number Estimate From Recalculated Composition - Subgroup Breakdowns as in Feed*	Total Aromatics Content wt.%
13	Syncrude Raffinate	Sulfur Dioxide	-11.5	1.5	1	39.6	38.5	23.28
37	Suncor "	" "	-12.0	1.0	1	43.7	43.2	19.57
102	Syncrude "	Acetonitrile	20	5.0	1	40.1	38.1	24.16
201	Suncor "	"	20	2.0	1	41.6	41.3	23.73
210	Syncrude "	Dimethyl Formamide	20	2.0	1	40.7	38.4	23.76
39	Suncor	" "	0	1.25	1	42.9	42.4	21.37
20-4	Syncrude "	Acetonitrile	20	2.0	2	39.6	37.3	26.07
20-9	" "	"	20	1.5	2	38.3	36.4	28.06
20-17	Suncor "	"	20	1.6	2	43.9	42.8	20.41
20-22	" "	"	20	1.6	2	43.8	42.3	21.66
24-004	Syncrude "	"	20	3.3	N.D.**	42.4	39.1	22.06
24-009	" "	"	20	3.3	N.D.	39.3	37.6	25.37
24-025	" "	"	20	3.3	N.D.	38.0	35.9	29.34
24-036	" "	"	20	3.3	N.D.	41.3	38.2	24.11
24-052	" "	"	20	3.3	N.D.	42.2	39.1	22.04

* The overall aromatics level is the same as in the actual raffinate

** N.D. Not determined

TABLE 4.28

Assumptions for the Economic Evaluation

Basis: 1000 bbl/day diesel produced from Syncrude middle distillate

- Extract density 0.91 g/mL @ 90% aromatics/10% saturates
- Raffinate density 0.85 g/mL @ 20% aromatics/80% saturates
- Approx. theoretical yield = 71 wt.% (72.4 vol.%)
- Theoretical height of transfer unit = 10' (4 required)
- Acetonitrile losses

(a) Diesel: 95% recovery of the 4 vol.% Acetonitrile in the overhead product = 2.0 bbl/day

(b) Aromatics: 5% aromatics in recycle solvent and 0.5% solvent in aromatics = 1.9 bbl/day

3.9 bbl/day

Total losses are projected at 1066 lb/day @ $0.75/lb
Daily acetonitrile make-up cost = $800.00/day
[versus 1000 bbl/day @ 0.6 vol.% D11-3 = $2623/day]

- Feed to overall process:
  - 45 vol.% middle distillate @ 32.6 °API
  - 55 vol.% Gas Oil @ 22.5 °API
  - Total feed rate = 3070 bbl/day @ 26.0 °API
  - Solvent makeup = 3.9 bbl/day Acetonitrile

- Products from overall process:
  - 1002 bbl/day 40 CN Diesel
  - 383 bbl/day Aromatic Extract

- Commodity Costs - Natural Gas @ $2.50/1000 scf.
  - Cooling Water @ $1.50/1000 IG
  - Steam @ $4.50/1000 lb.
  - Diesel Ignition Improver @ $1.25/lb
  - Acetonitrile @ $0.74/lb

- Plant 100 & 200 are supplied by on-site utilities and control rooms are integrated into existing facilities. Diesel product storage is already available on-site. Construction period is one year from capital commitment.

TABLE 4.29

Equipment List

NOTE: Equipment Cost = Unit Cost (in year n) X Materials of Construction Factor X Total Installation Factor X Cost Index $\frac{\text{M\&S 1986}}{\text{M\&S Year n}}$

1. Process Heaters

H101 Heat 26° API total gas oil from 450°F to 640°F for 60% flash
Enthalpy + 285 Btu/lb @ 450°F & 470 Btu/lb @ 640°F
∴ Duty = 185 Btu/lb x 40276 lb/hr = 7.45 MM Btu/hr
Energy required @ 80% heater eff. = 9.31 MM Btu/hr
Natural Gas equivalent = 0.224 MMSCF/day

Equipment cost = \$27,000 x 1.75 x 2.27 x $\frac{856}{273}$ = \$336,310.00

H201 Heat 35° API middle distillate (4 vol.% acetonitrile) from 68°F to 400°F
Enthalpy = 95 Btu/lb @ 68°F & 290 Btu/lb @ 400°F
∴ Duty = 195 Btu/lb x 12,850 lb = 2.51 MM Btu/hr
Energy required @ 80% efficiency = 3.13 MM Btu/hr
Natural Gas equivalent = 0.075 MMSCF/day

Equipment cost = \$11,000 x 1.75 x 2.27 x $\frac{856}{273}$ = \$137,015.00

2. Vessels

V101 40-tray distillation tower 4' dia. x 42' length
stainless steel trays and stainless clad interior

Equipment cost \$9,500 x 2.25 x 4.23 x $\frac{856}{273}$ = \$283,503.00 vessel

1,200 x 5.7 x $\frac{856}{273}$ = 21,447.00 tray

\$304,950.00

V201 40-tray extraction column. Assume loading @ 90% of flood rate (approx. 60 $ft^3/ft^2/hr$) = 54 $ft^3/ft^2/hr$
Based on a 2:1 solvent/oil ratio the feed rate = 970 ft^3/hr
∴ 18.0 ft^2 required
Column diameter approx. 5' x 42' length
Equipment cost \$12,500 x 2.25 x 4.23 x $\frac{856}{273}$ = \$373,030.00 vessel cost

2,000 x 5.7 x 2.0 x $\frac{856}{273}$ = \$ 71,490.00 tray cost

\$444,520.00

TABLE 4.29 (cont'd)

V202 Raffinate Separator: 1 hour holdup, 80% working volume
approx. 2400 USG, 6' dia x 12' length

Equipment cost $\$3,000 \times 2.25 \times 3.18 \times \frac{856}{273} = \$\ 67,304.00$

V203 Extract Separator: 1 hour holdup, 80% working volume
approx. 6000 USG, 8' dia x 16' length

Equipment cost $\$5,000 \times 2.25 \times 3.18 \times \frac{856}{273} = \$112,174.00$

V204 Raffinate Fractionator: 20-tray column
approx. 2' dia. x 24' length stainless clad & stainless trays

Equipment cost $\$2,500 \times 2.25 \times 4.23 \times \frac{856}{273} = \$74,606.00$ vessel cost

$\$325 \times 5.7 \times \frac{856}{273} = 5,809.00$ tray cost

$\$80,415.00$

V205 Solvent Recovery Unit: 20-tray column
approx. 4' dia. x 24' length

Equipment Cost $\$6,000 \times 2.25 \times 4.23 \times \frac{856}{273} = \$179,054.00$ vessel cost

$\$700 \times 5.7 \times \frac{856}{273} = \$\ 12,511.00$ tray cost

$\$191,565.00$

Heat Exchangers

E101 5.6 MM Btu/hr Duty: Shell & Tube Condenser
approx. U = 70 Btu/ft^2/hr °F

$A = \frac{Q}{U\Delta T} = \frac{5.6\ MM}{70 \times 150} = 520\ ft^2$

Equipment cost = $\$5,000 \times 2.25 \times 3.29 \times \frac{856}{273} = \$116,054.00$

E102 3.3 MM Btu/hr Duty: Shell & Tube Cooler
approx. U = 60 Btu/ft^2/hr °F

$A = \frac{3.3\ MM}{60 \times 382} = 150\ ft^2$

Equipment cost = $\$3,100 \times 2.25 \times 3.29 \times \frac{856}{273} = \$\ 71,954.00$

E103 0.5 MM Btu/hr Duty: Shell & Tube Reboiler

$U = 60\ Btu/ft^2/hr, °F$

$A = \frac{0.5\ MM}{60 \times 25} = 350\ ft^2$

Equipment cost = $\$4,500 \times 2.25 \times 3.29 \times \frac{856}{273} = \$104,448.00$

TABLE 4.29 (cont'd)

E104 4.4 MM Btu/hr Duty: Shell & Tube Cooler

$U = 70$ Btu/ft^2/hr °F

$A = \frac{4.4 \text{ MM}}{70 \times 350} = 180$ ft^2 = $ 76,596.00

E201 Solvent Condenser

0.4 MM Btu/hr Duty: Shell & Tube

$U = 70$ Btu/ft^2/hr °F

$A = \frac{0.4}{70 \times 120}$ MM = 50 ft^2

Equipment cost = $1000 x 2.25 x 3.29 x $\frac{856}{273}$ = $23,210.00

E202 Product Cooler

1.4 MM Btu/hr Duty: Shell & Tube

$U = 70$ Btu/ft^2/hr °F

$A = \frac{1.4}{70 \times 200}$ MM = 100 ft^2

Equipment cost = $2000 x 2.25 x 3.29 x $\frac{856}{273}$=$46,425.00

E203 Solvent Condenser

5.0 MM Btu/hr Duty: Shell & Tube

$U = 75$ Btu/ft^2/hr °F

$A = \frac{5.0}{75 \times 50}$ MM = 1350 ft^2

Equipment cost = $11,000 x 2.25 x 3.29 x $\frac{856}{273}$ = $255,318.00

E204 Solvent Cooler

2.2 MM Btu/hr Duty: Shell & Tube

$U = 70$ Btu/ft^2/hr °F

$A = \frac{2.2}{70 \times 132}$ MM = 240 ft^2

Equipment cost = $3,600 x 2.25 x 3.29 x $\frac{856}{273}$ = $ 83,560.00

TABLE 4.29 (cont'd)

E205 Solvent Recovery Reboiler
0.5 MM Btu/hr Duty: Shell & Tube
U = 70 Btu/ft^2/hr °F
$A = \frac{0.5}{70 \times 50}$ MM = 150 ft^2

Equipment cost = $3,100 x 2.25 x 3.29 x $\frac{856}{273}$ = $ 71,954.00

E206 Solvent Recovery Heater
6.8 MM Btu/hr Duty: Shell & Tube
U = 65 Btu/ft^2/hr °F
$A = \frac{6.8}{65 \times 182}$ MM = 600 ft^2

Equipment cost = $6,400 x 2.25 x 3.29 x $\frac{856}{273}$ = $148,550.00

Pumps

P101 Gas Oil Transfer Pump
60 USGPM @ ΔP = 50 psi @ 70% eff.
Requires 2.5 Hp driver
Equipment cost = $700 x 1.93 x 3.38 x $\frac{856}{273}$ = $ 14,318.00

P102 Middle Distillate Transfer Pump
40 USGPM @ ΔP = 100 psi @ 70% eff.
Requires 3.5 Hp driver
Equipment cost = $800 x 1.93 x 3.38 x $\frac{856}{273}$ = $ 16,364.00

P201 Overhead Solvent Recycle
3 USGPM @ ΔP = 50 psi @ 70% eff.
Requires 1/4 Hp, driver
Equipment cost = $350 x 1.93 x 3.38 x $\frac{856}{273}$ = $ 7,159.00

P202 Solvent Recycle Main Pump
80 USGPM @ ΔP = 100 psi @ 70% eff.
Requires 7 Hp driver
Equipment cost = $1,000 x 1.93 x 3.38 x $\frac{856}{273}$ = $ 20,454.00

TABLE 4.30

COST SUMMARY

1986 Canadian Dollars*

1. (a)	Total Installed Equipment Cost, Plant 100		= $3,206,538.00
(b)	Total Installed Equipment Cost, Plant 200		= $5,068,869.00
2. (a)	Total Operating Cost, Plant 100		
	Natural Gas	$ 560/SD**	
	Cooling Water	$1,915/SD	
	Steam	$ 540/SD	
	Staff @ 5 man-years	$ 5,000/SD	= $2,404,500.00/year
(b)	Total Operating Cost, Plant 200		
	Natural Gas	$ 187.5/SD	
	Cooling Water	$ 1,296/SD	
	Steam	$ 7,884/SD	
	Staff @ 3 man-years	$ 3,000/SD	
	Acetonitrile makeup	$ 800.00/SD	= $3,950,250.00/year
3. (a)	Working Capital, Plant 100		= $0.0
(b)	Working Capital, Plant 200 (3000 bbl solvent)		= $615,100.00

* (1986 U.S. Gulf Coast to 1986 Canadian Northern Alberta Factor = 3.0)
**SD = Stream Day (300 days/year)

FIGURE 2.1

SOLVENT EXTRACTION APPARATUS

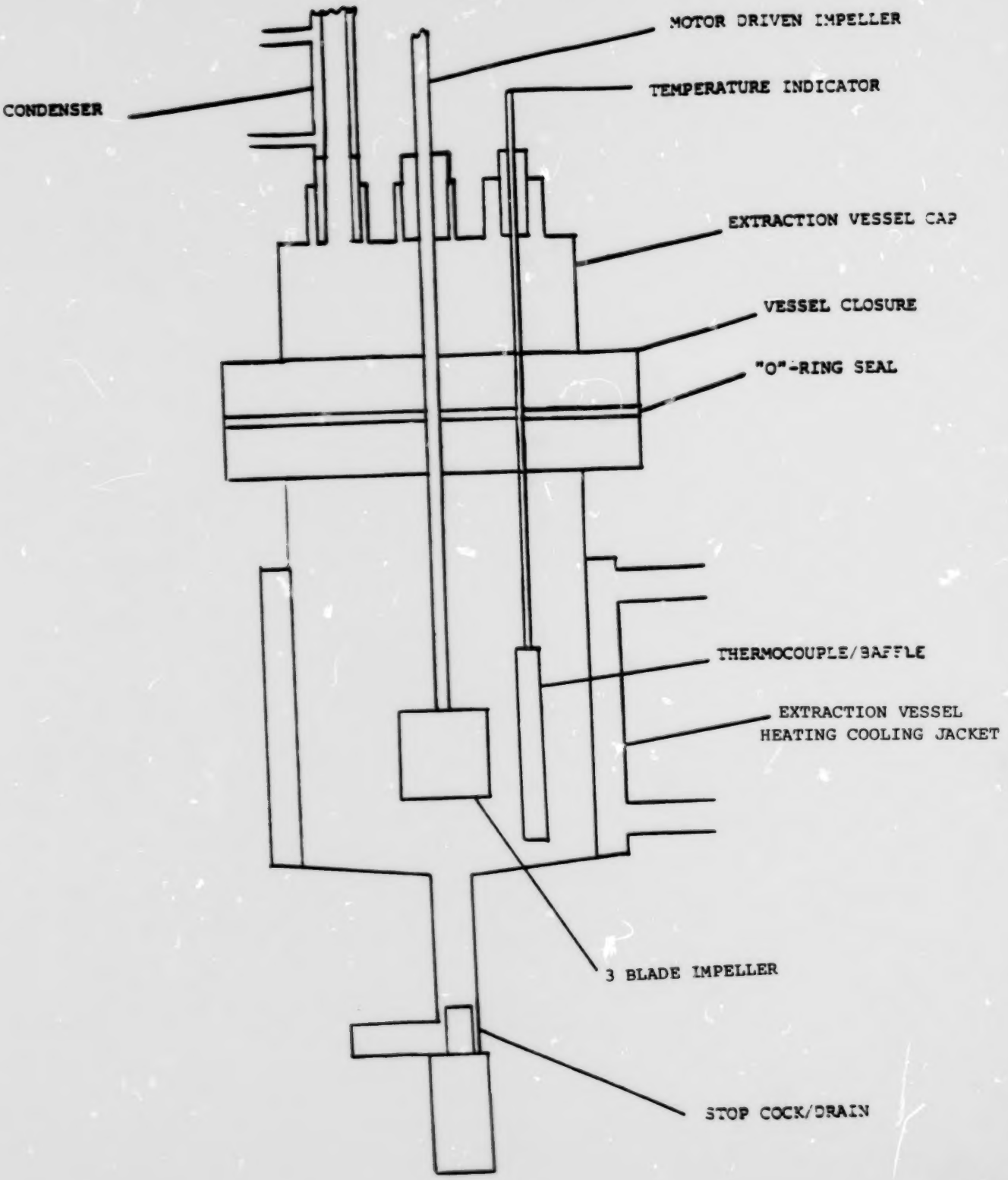
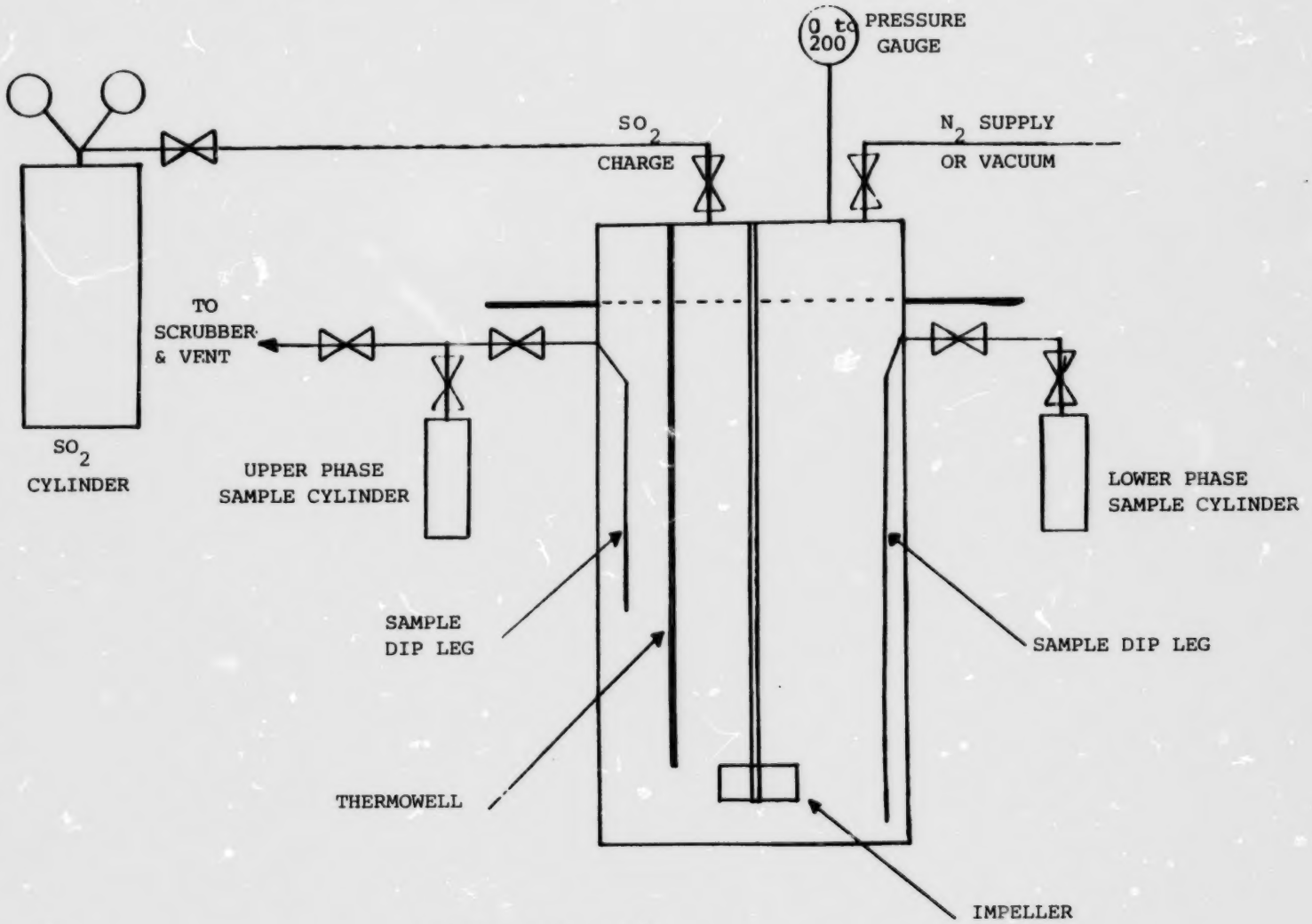


FIGURE 2.2

EXTRACTION APPARATUS FOR SO_2 EXPERIMENTS



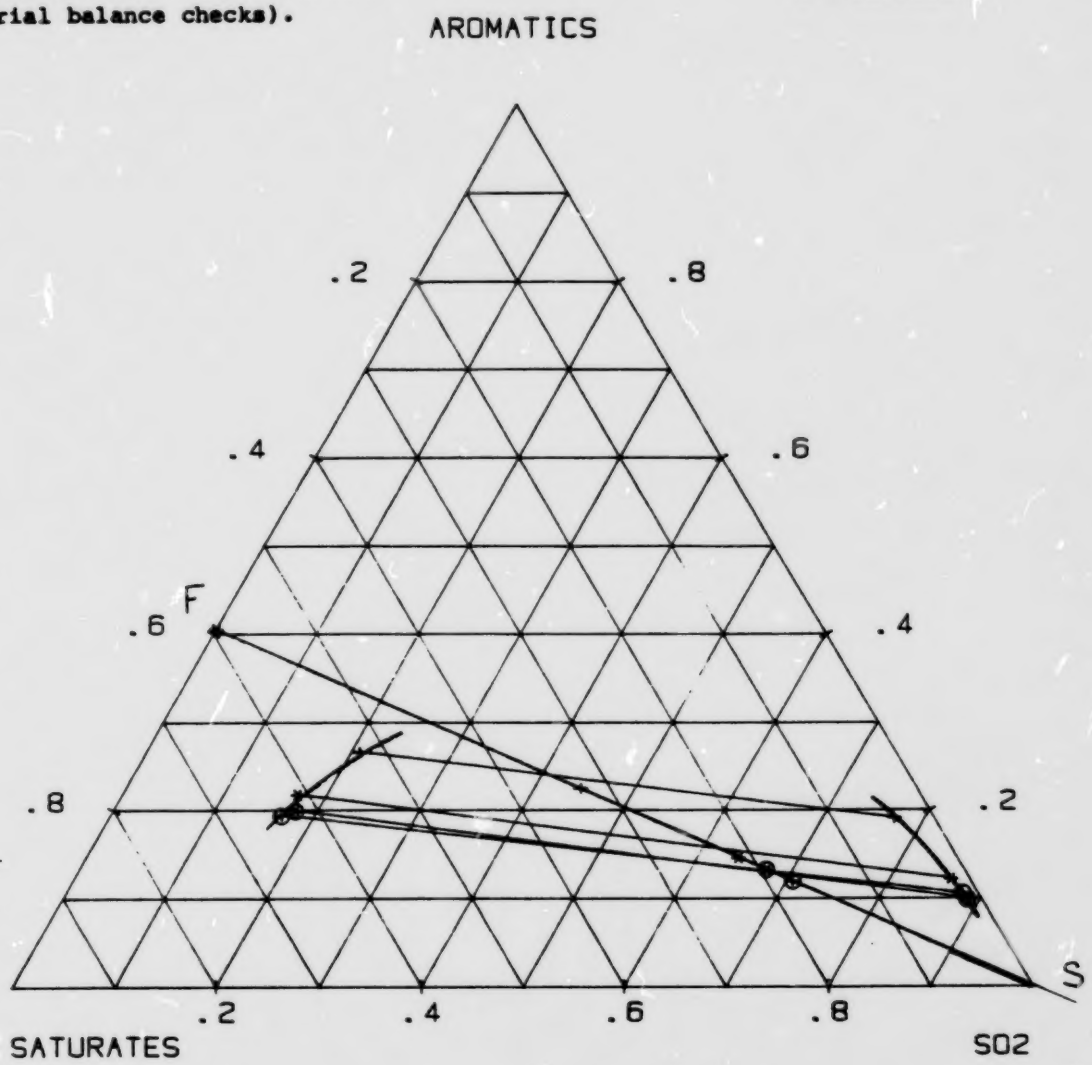
1-LITRE AUTOCLAVE

+ Nominal solvent/oil ratio = 0.5 (vol/vol)
* " " " " = 1.0 "
◉ " " " " = 1.25 "
⊕ " " " " = 1.5 "

FIGURE 4.1

End points of the tie-lines are equilibrium phase compositions, the other four points represent the feed + solvent mixtures at the corresponding solvent/oil ratios (material balance checks).

F = Feed
S = Solvent



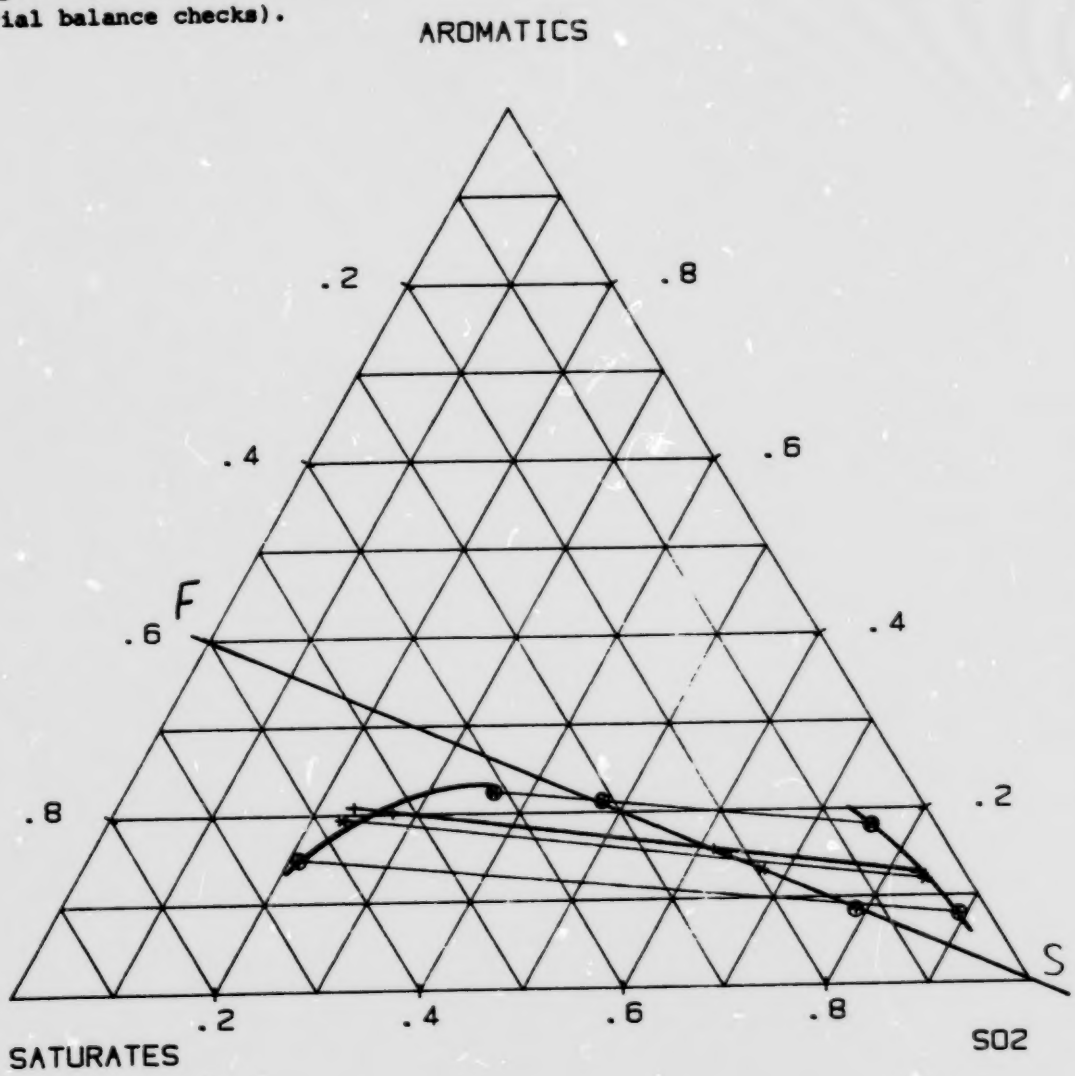
TIE-LINES AND MATERIAL BALANCE CHECKS
FOR SO2 EXTRACTION OF
SYNCRUDE MIDDLE DISTILLATE
AT (APPROXIMATELY) -12C

⊙ Nominal solvent/oil ratio = 0.5 (vol/vol)
\+ " " " " = 1.0 " (replicate experiments)
* " " " " = 1.25 "
⊕ " " " " = 2.0 "

FIGURE 4.2

End points of the tie-lines are equilibrium phase compositions, the other five points represent the feed + solvent mixtures at the corresponding solvent/oil ratios (material balance checks).

F = Feed
S = Solvent



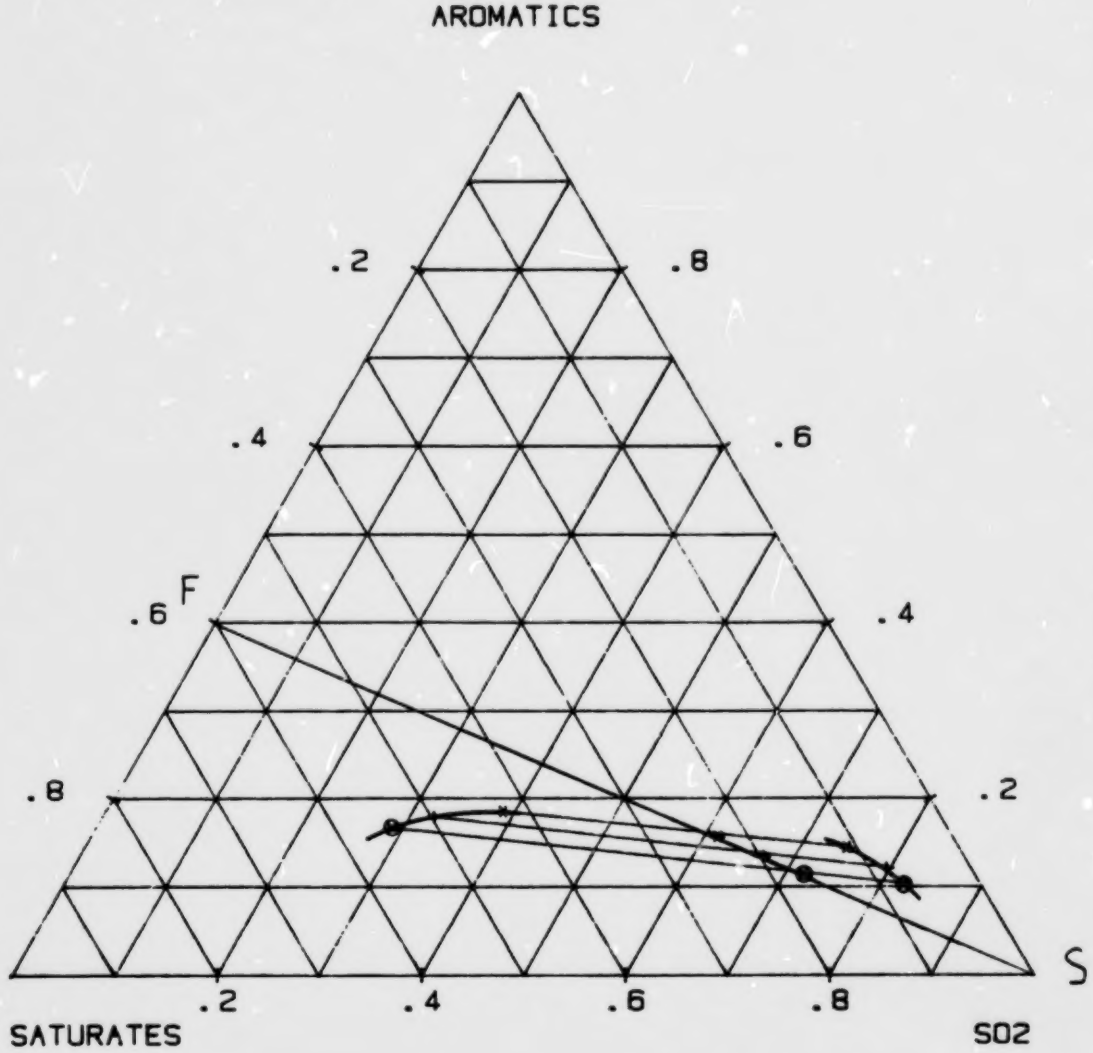
TIE-LINES AND MATERIAL BALANCE CHECKS
FOR SO2 EXTRACTION OF
SYNCRUDE MIDDLE DISTILLATE
AT (APPROXIMATELY) 2C

* Nominal solvent/oil ratio = 1.0 (vol/vol)
\+ " " " " = 1.25 "
⊛ " " " " = 1.5 "

End points of the tie-lines are equilibrium phase compositions, the other three points represent the feed + solvent mixtures at the corresponding solvent/oil ratios (material balance checks).

FIGURE 4.3

F = Feed
S = Solvent

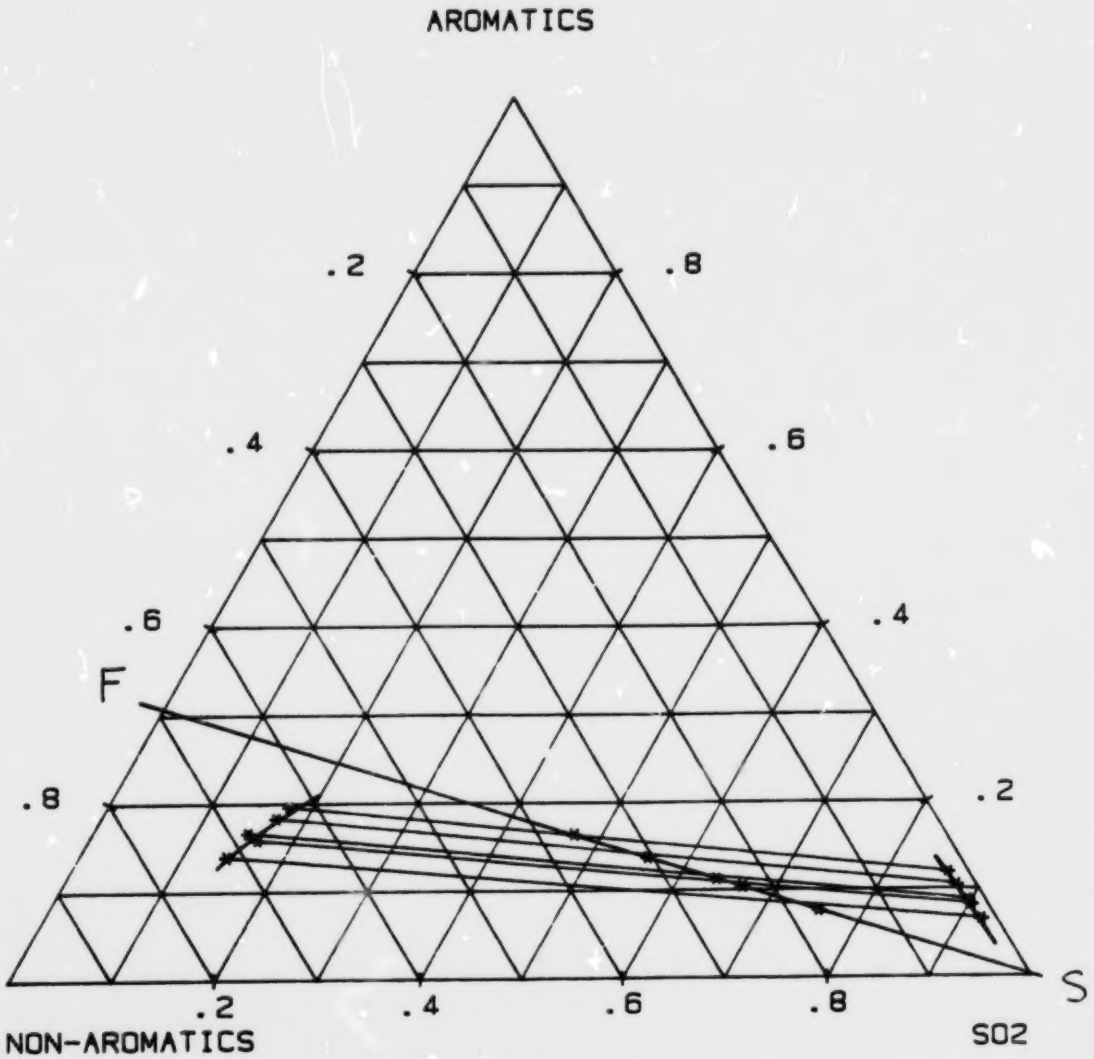


TIE-LINES AND MATERIAL BALANCE CHECKS
FOR SO2 EXTRACTION OF
SYNCRUDE MIDDLE DISTILLATE
AT (APPROXIMATELY) 17C

End points of the tie-lines are equilibrium phase compositions, the other five points represent the feed + solvent mixtures at the corresponding solvent/oil ratios (material balance checks).

FIGURE 4.4

F = Feed
S = Solvent

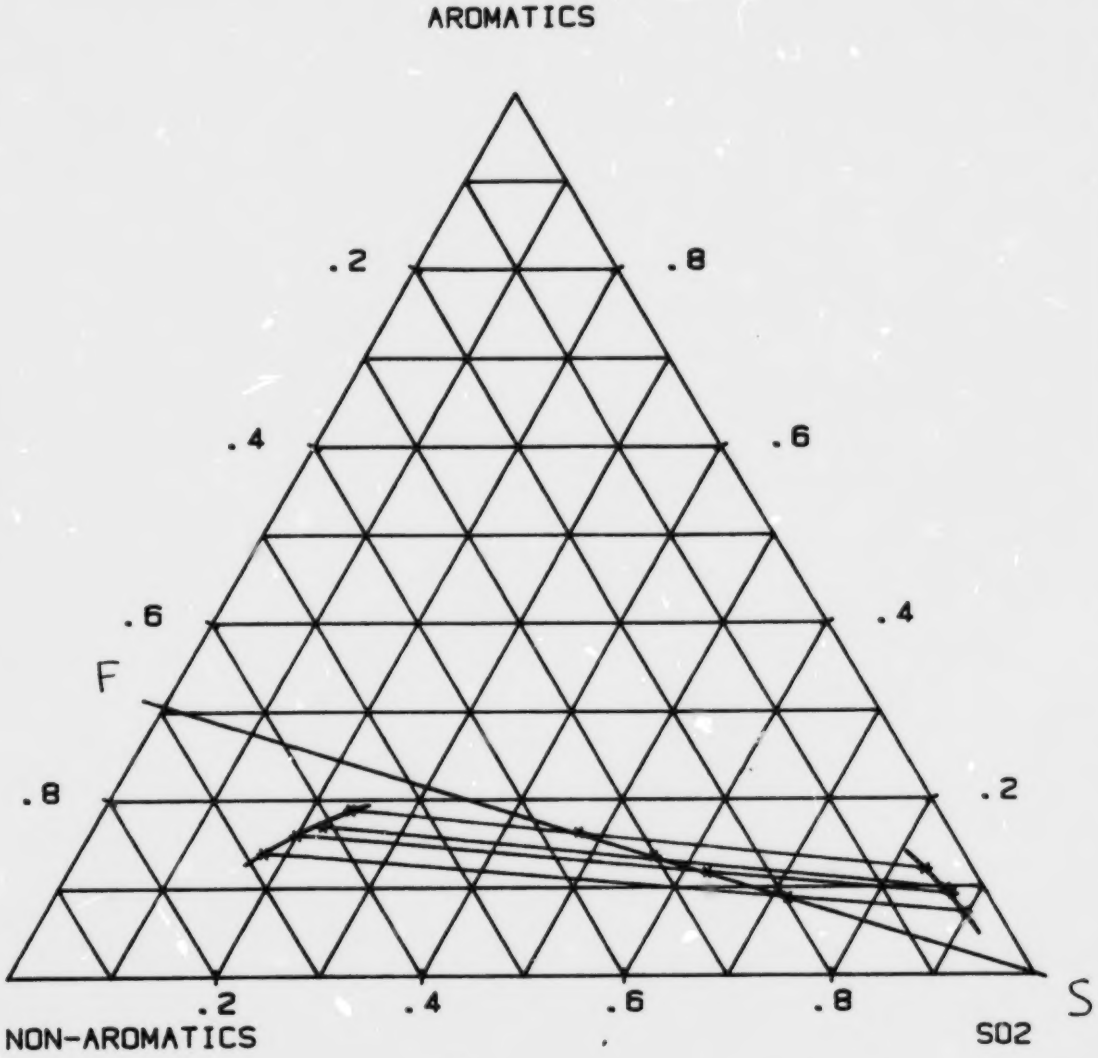


TIELINES AND MATERIAL BALANCE CHECKS
FOR SO2 EXTRACTION OF
SUNCOR MIDDLE DISTILLATE
AT (APPROXIMATELY) -12C

End points of the tie-lines are equilibrium phase compositions, the other four points represent the feed + solvent mixtures at the corresponding solvent/oil ratios (material balance checks).

FIGURE 4.5

F = Feed
S = Solvent

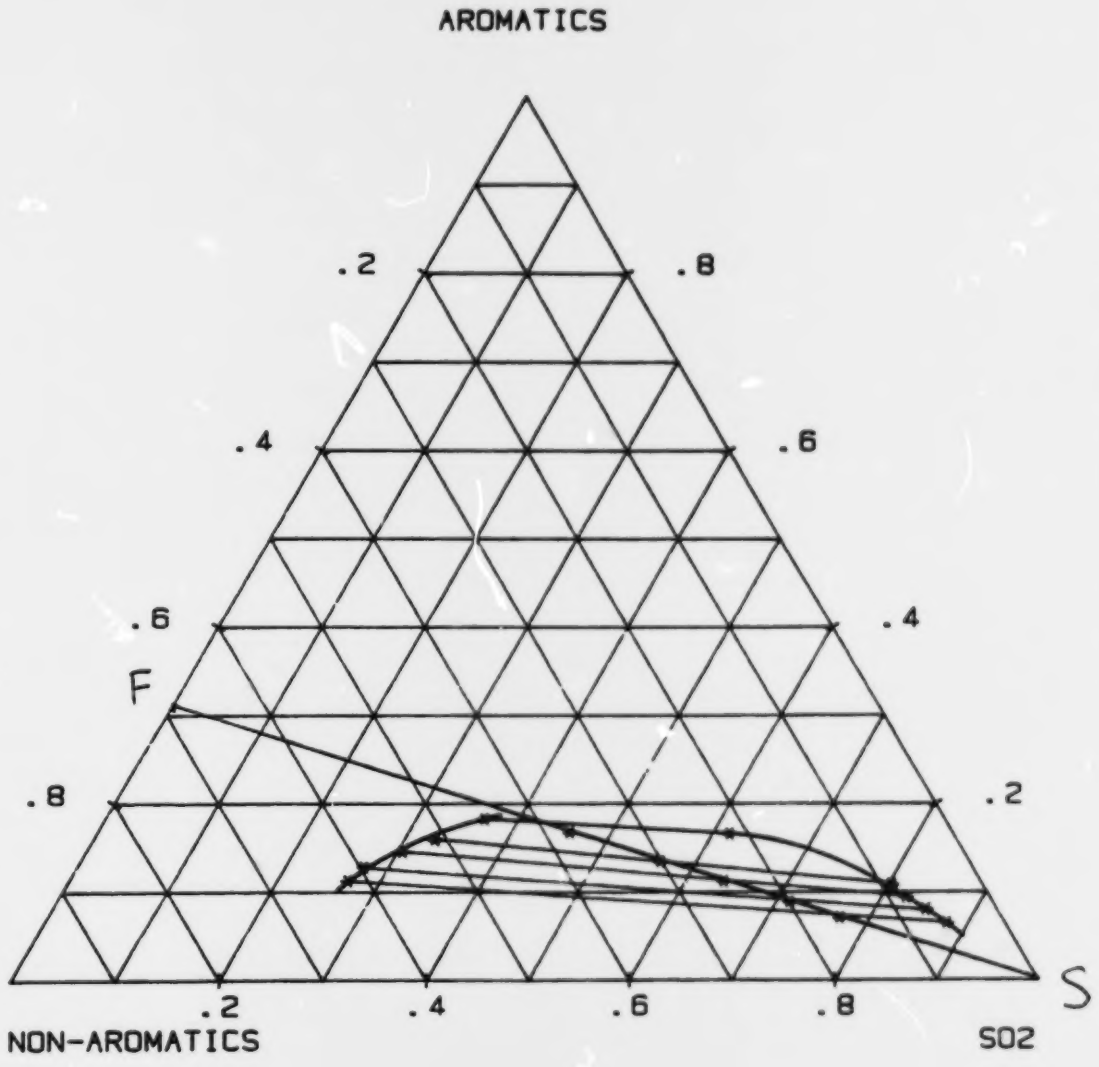


TIELINES AND MATERIAL BALANCE CHECKS
FOR SO2 EXTRACTION OF
SUNCOR MIDDLE DISTILLATE
AT (APPROXIMATELY) 2.5C

End points of the tie-lines are equilibrium phase compositions, the other five points represent the feed + solvent mixtures at the corresponding solvent/oil ratios (material balance checks).

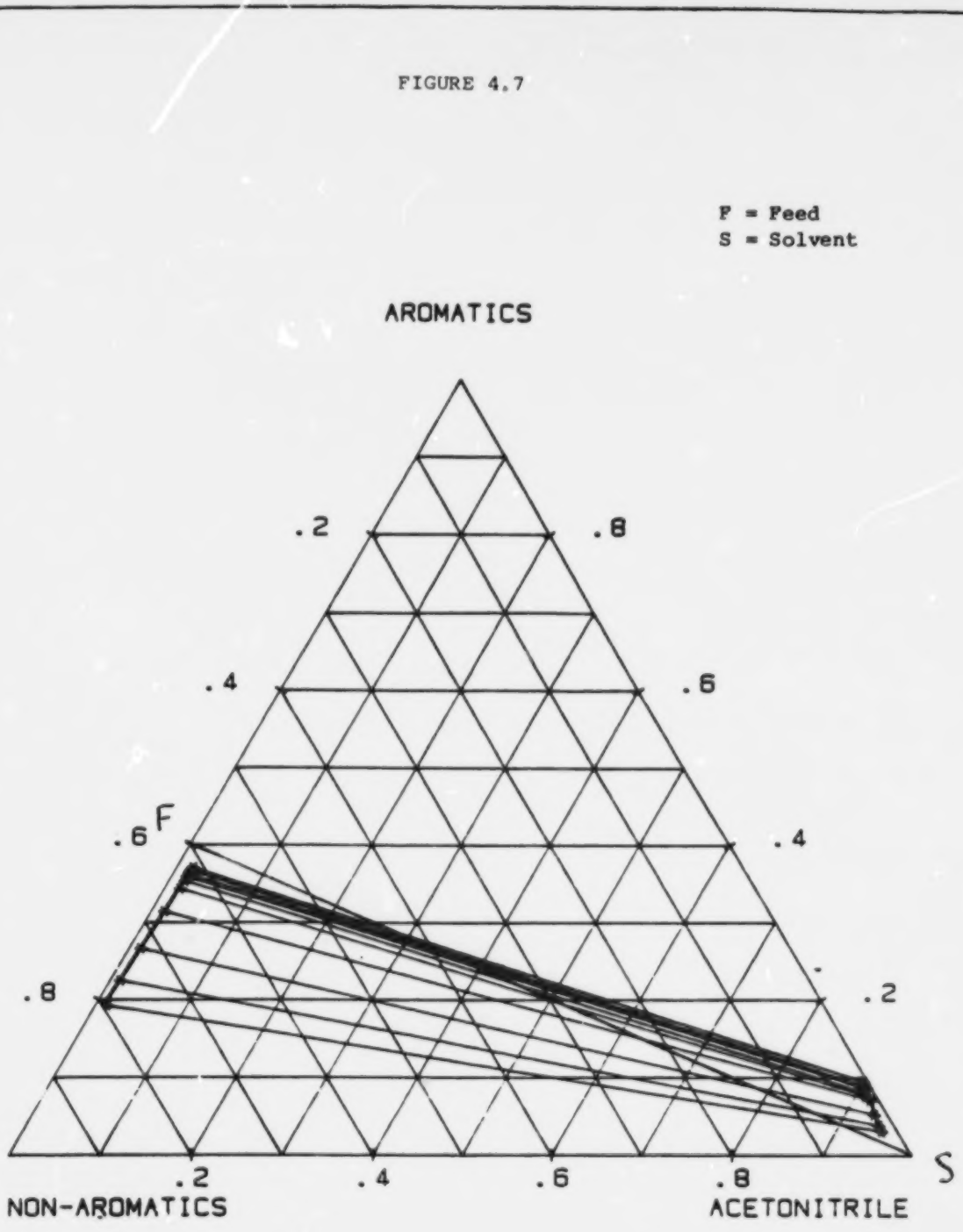
FIGURE 4.6

F = Feed
S = Solvent



TIELINES AND MATERIAL BALANCE CHECKS
FOR SO2 EXTRACTION OF
SUNCOR MIDDLE DISTILLATE
AT (APPROXIMATELY) 17.5C

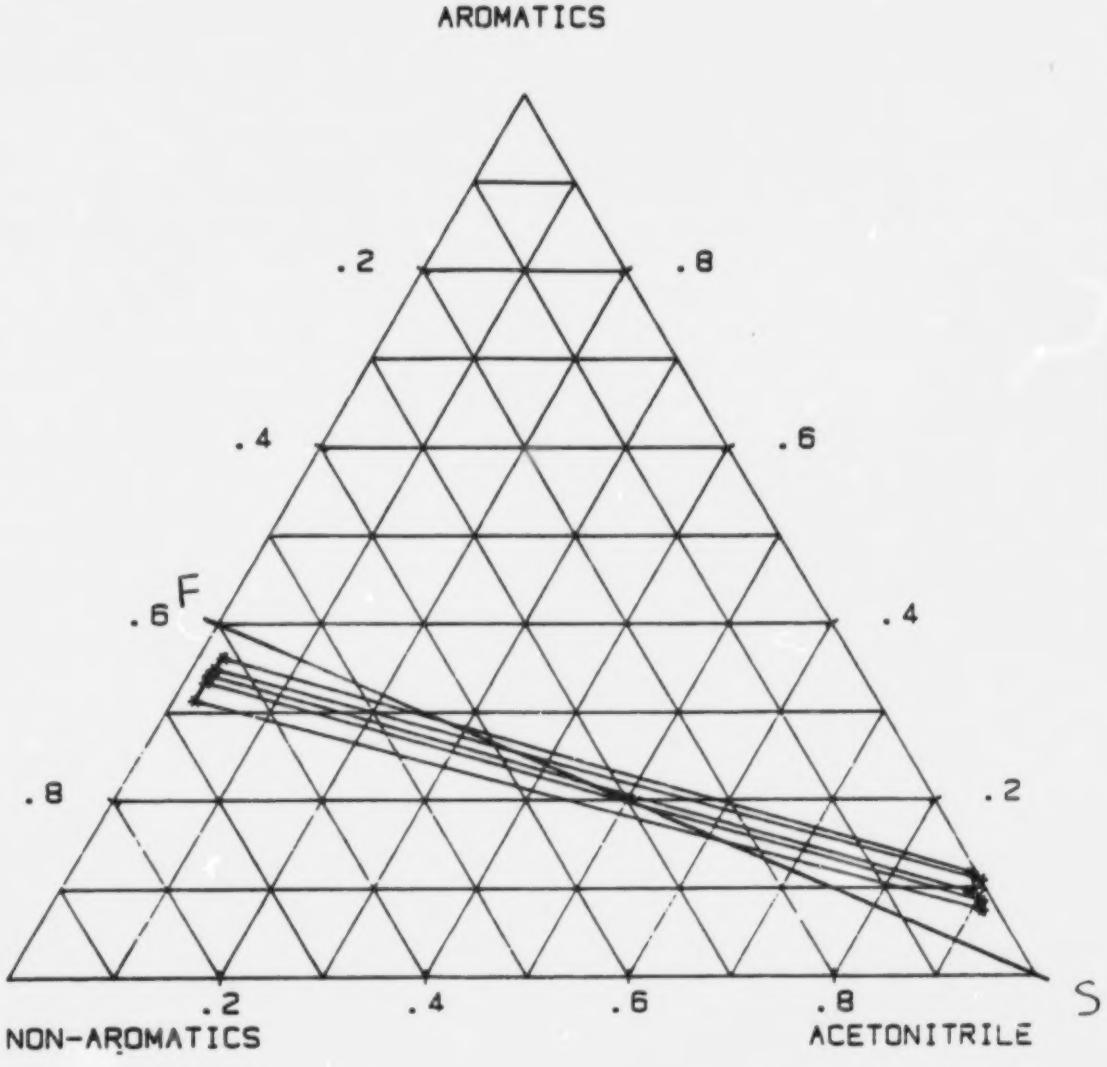
FIGURE 4.7



TIE-LINES FOR ACETONITRILE EXTRACTION
OF SYNCRUDE MIDDLE DISTILLATE
AT (APPROXIMATELY) 0C

FIGURE 4.8

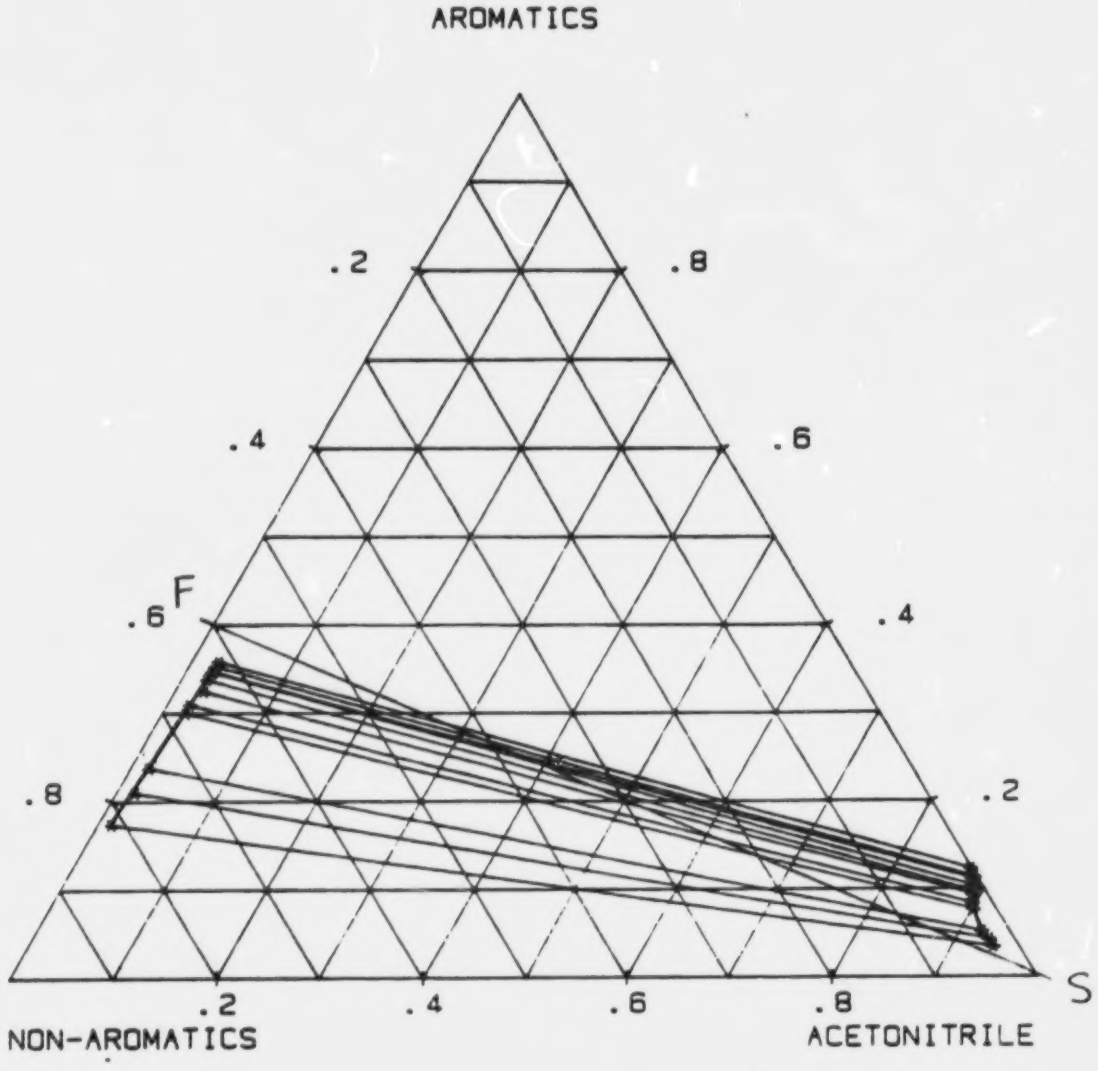
F = Feed
S = Solvent



TIE-LINES FOR ACETONITRILE EXTRACTION
OF SYNCRUDE MIDDLE DISTILLATE
AT (APPROXIMATELY) 12C

FIGURE 4.9

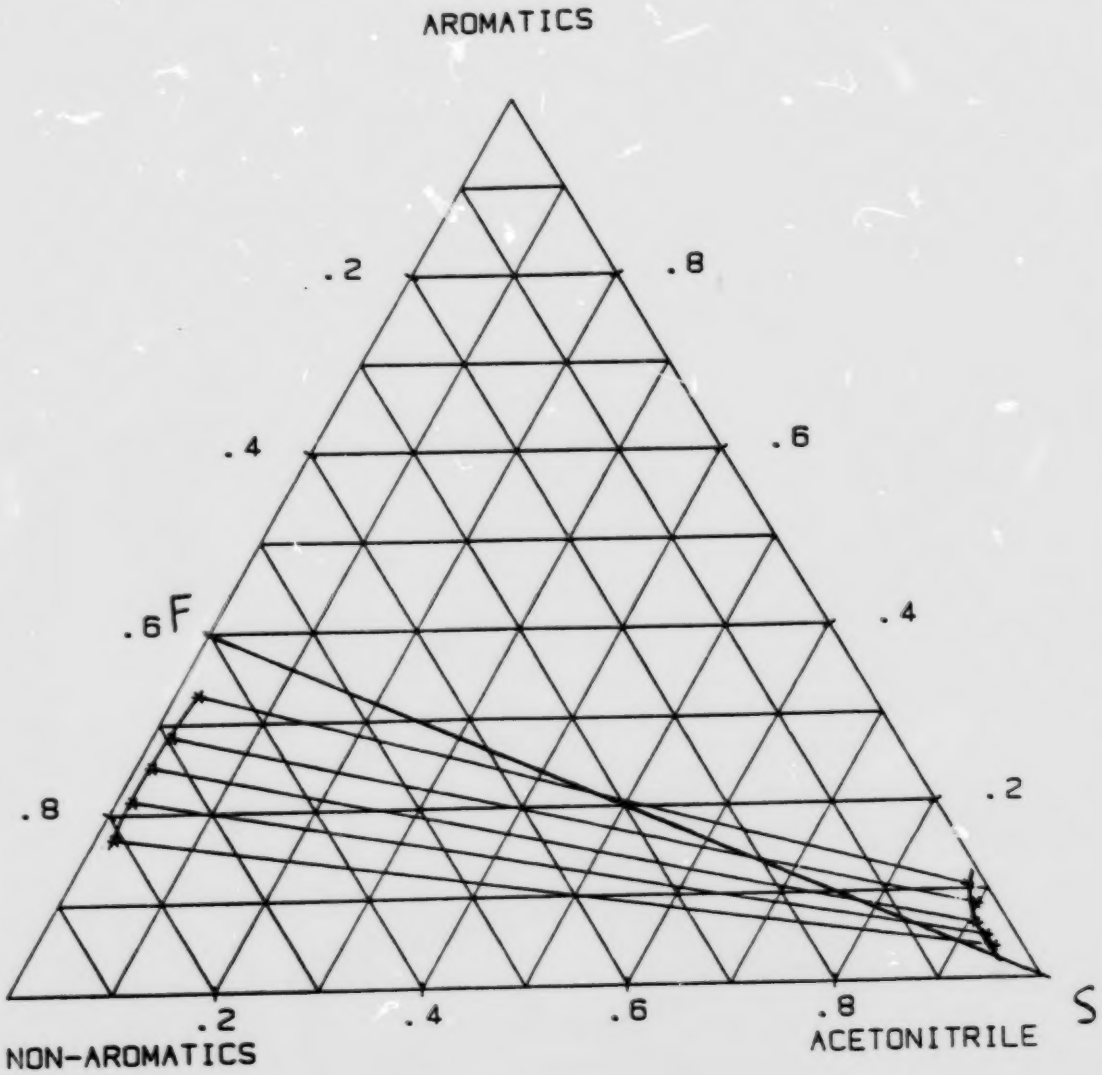
F = Feed
S = Solvent



TIE-LINES FOR ACETONITRILE EXTRACTION
OF SYNCRUDE MIDDLE DISTILLATE
AT (APPROXIMATELY) 20C

FIGURE 4.10

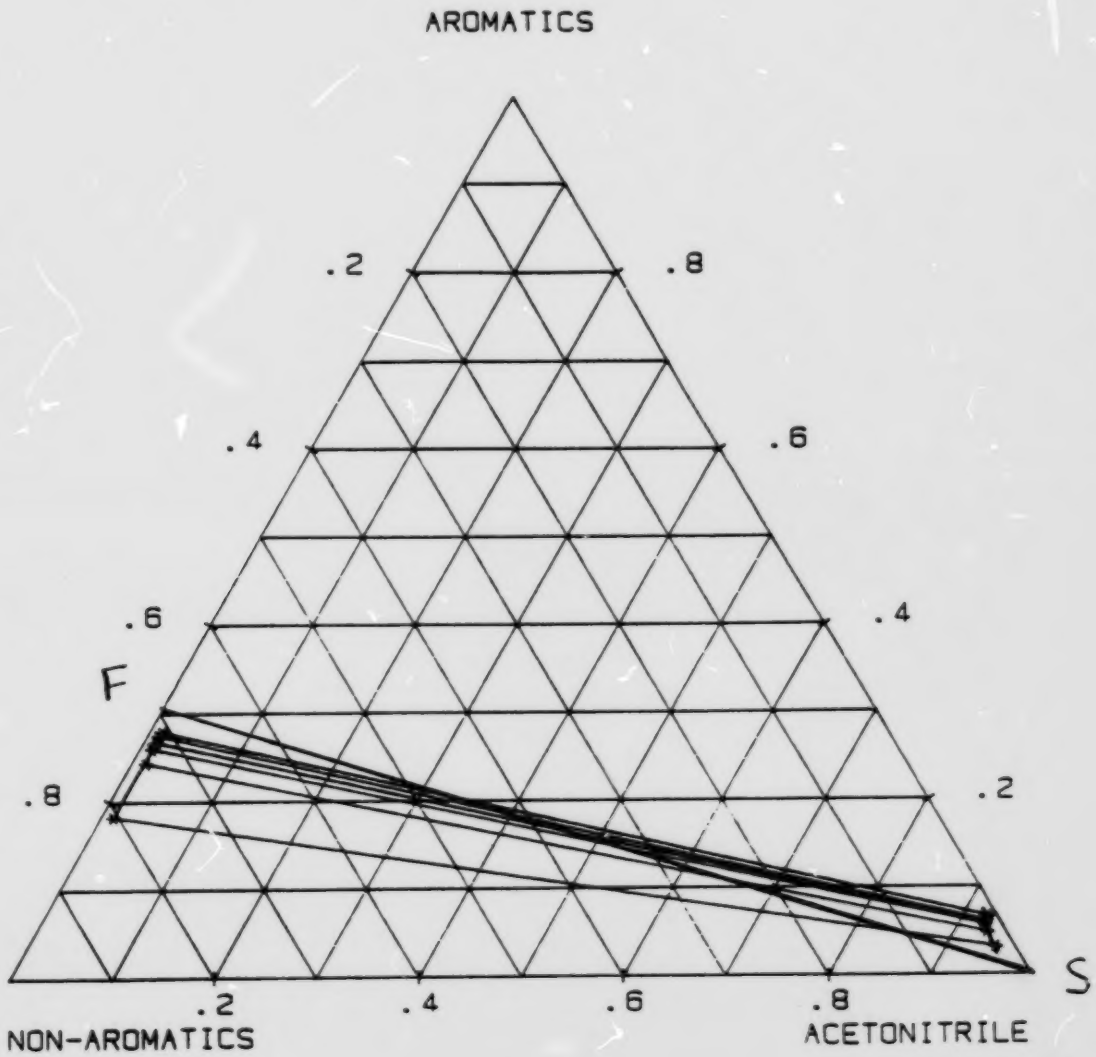
F = Feed
S = Solvent



TIELINES FOR ACETONITRILE EXTRACTION
OF SYNCRUDE MIDDLE DISTILLATE
AT (APPROXIMATELY) 30C

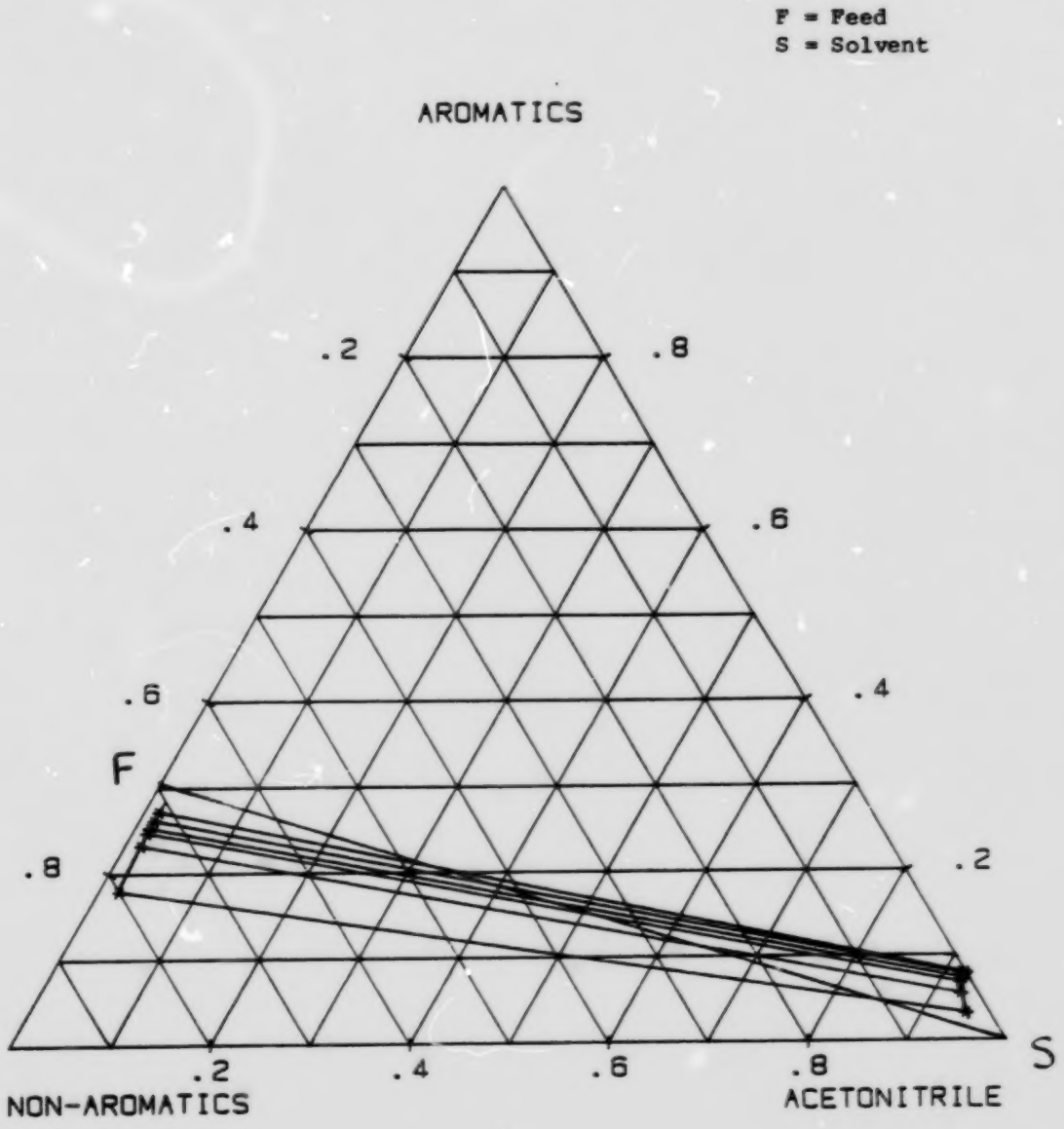
FIGURE 4.11

F = Feed
S = Solvent



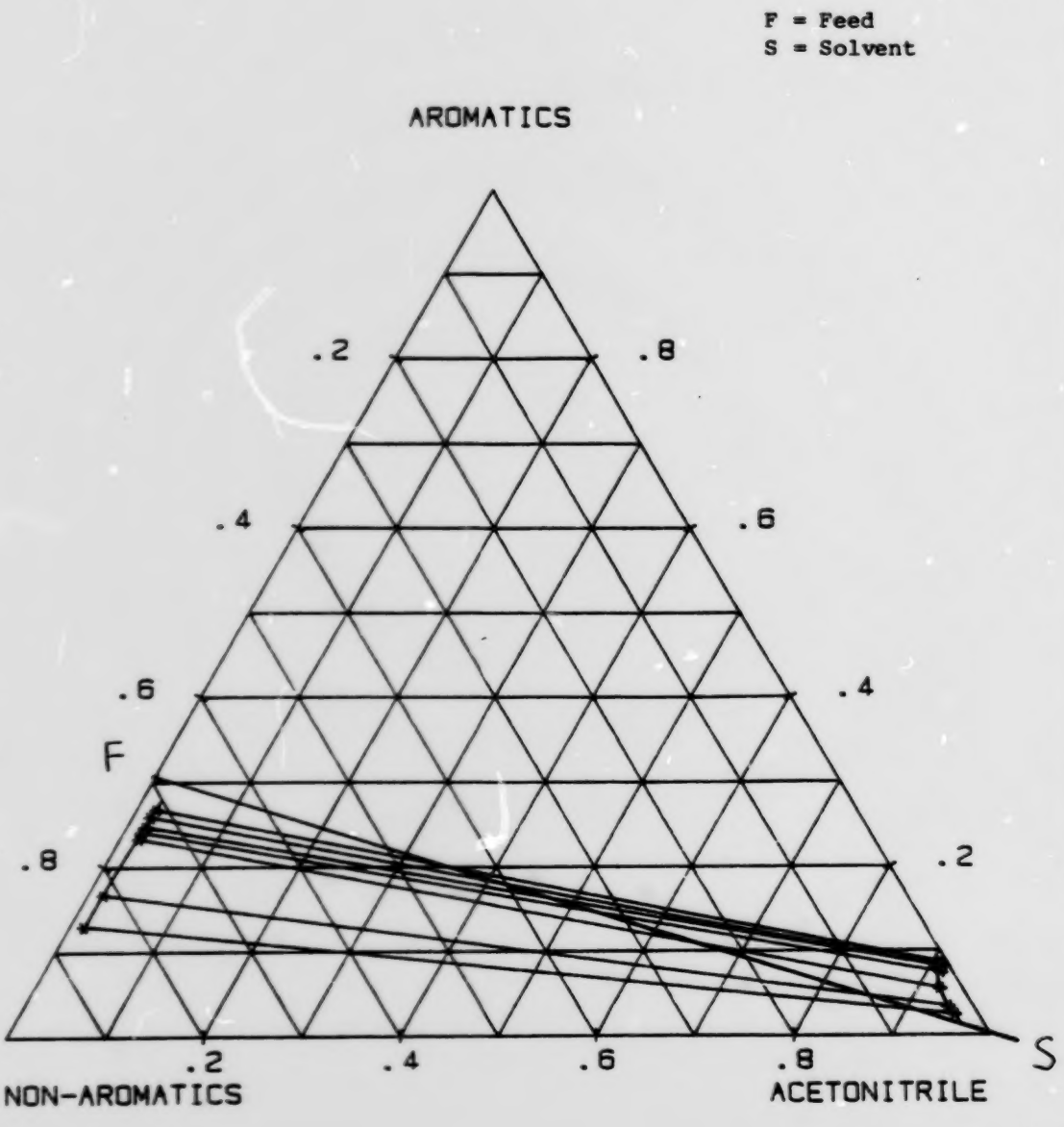
TIELINES FOR ACETONITRILE EXTRACTION
OF SUNCOR MIDDLE DISTILLATE
AT (APPROXIMATELY) 0C

FIGURE 4.12



TIELINES FOR ACETONITRILE EXTRACTION
OF SUNCOR MIDDLE DISTILLATE
AT (APPROXIMATELY) 10C

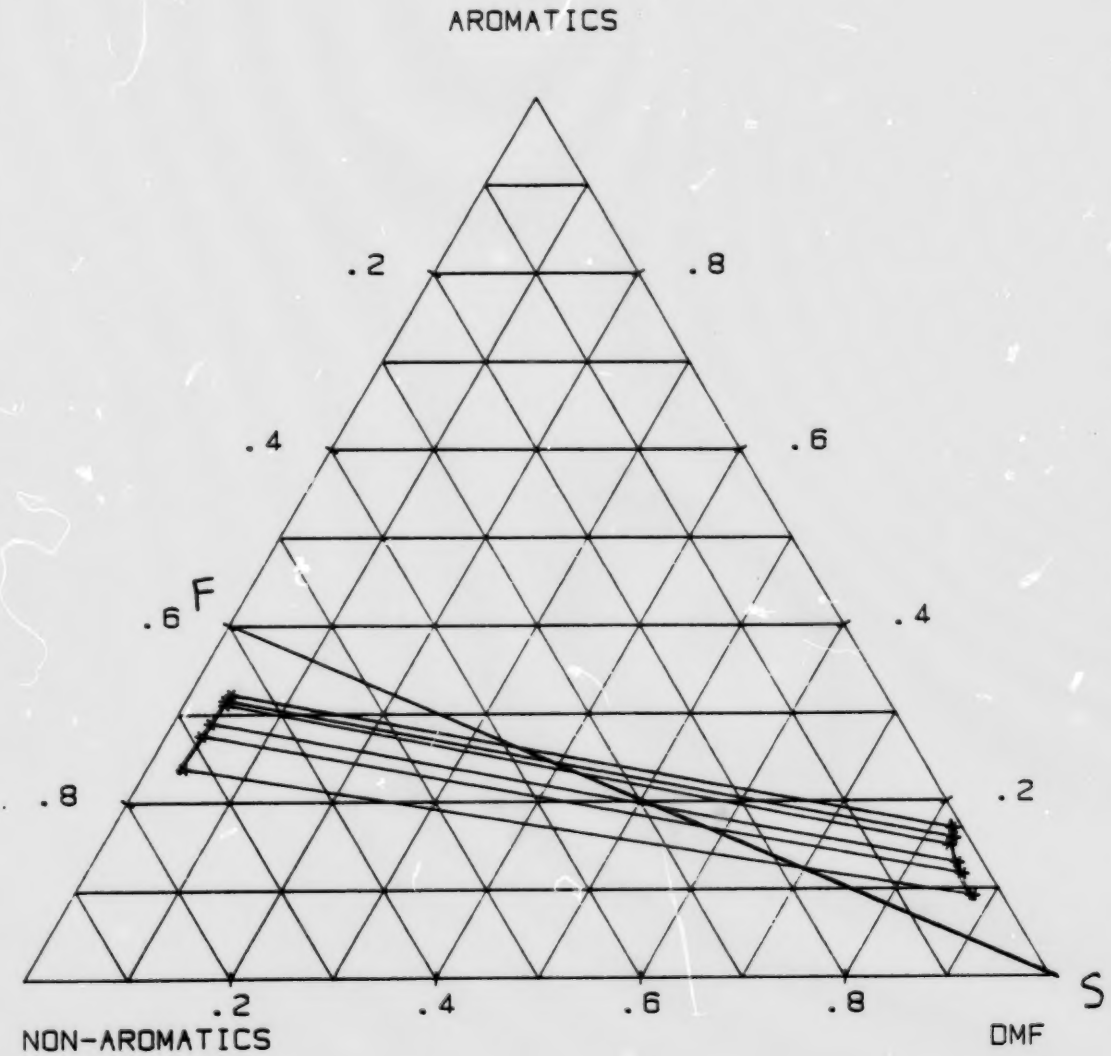
FIGURE 4.13



TIELINES FOR ACETONITRILE EXTRACTION
OF SUNCOR MIDDLE DISTILLATE
AT (APPROXIMATELY) 20C

FIGURE 4.14

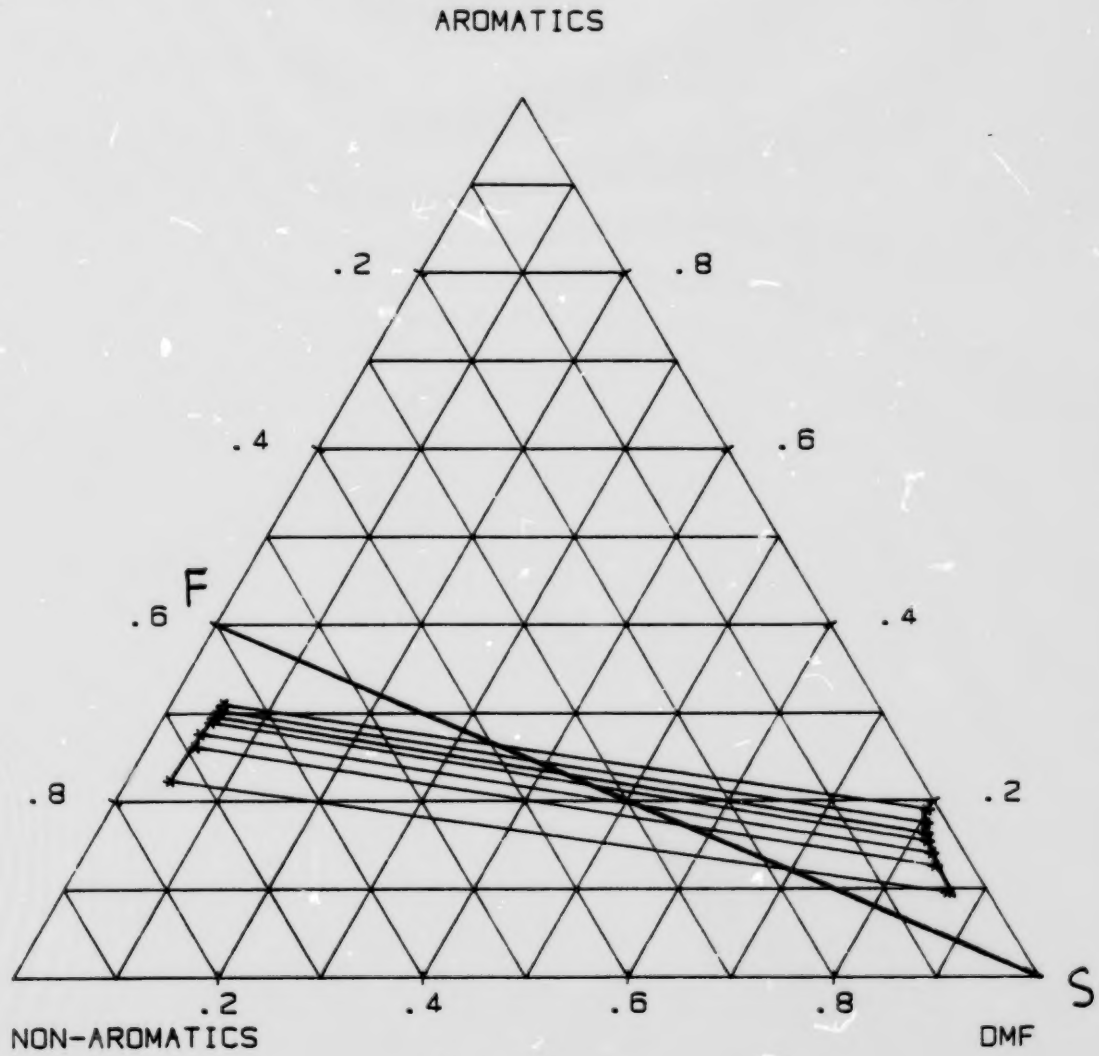
F = Feed
S = Solvent



TIELINES FOR DMF EXTRACTION
OF SYNCRUDE MIDDLE DISTILLATE
AT (APPROXIMATELY) 0C

FIGURE 4.15

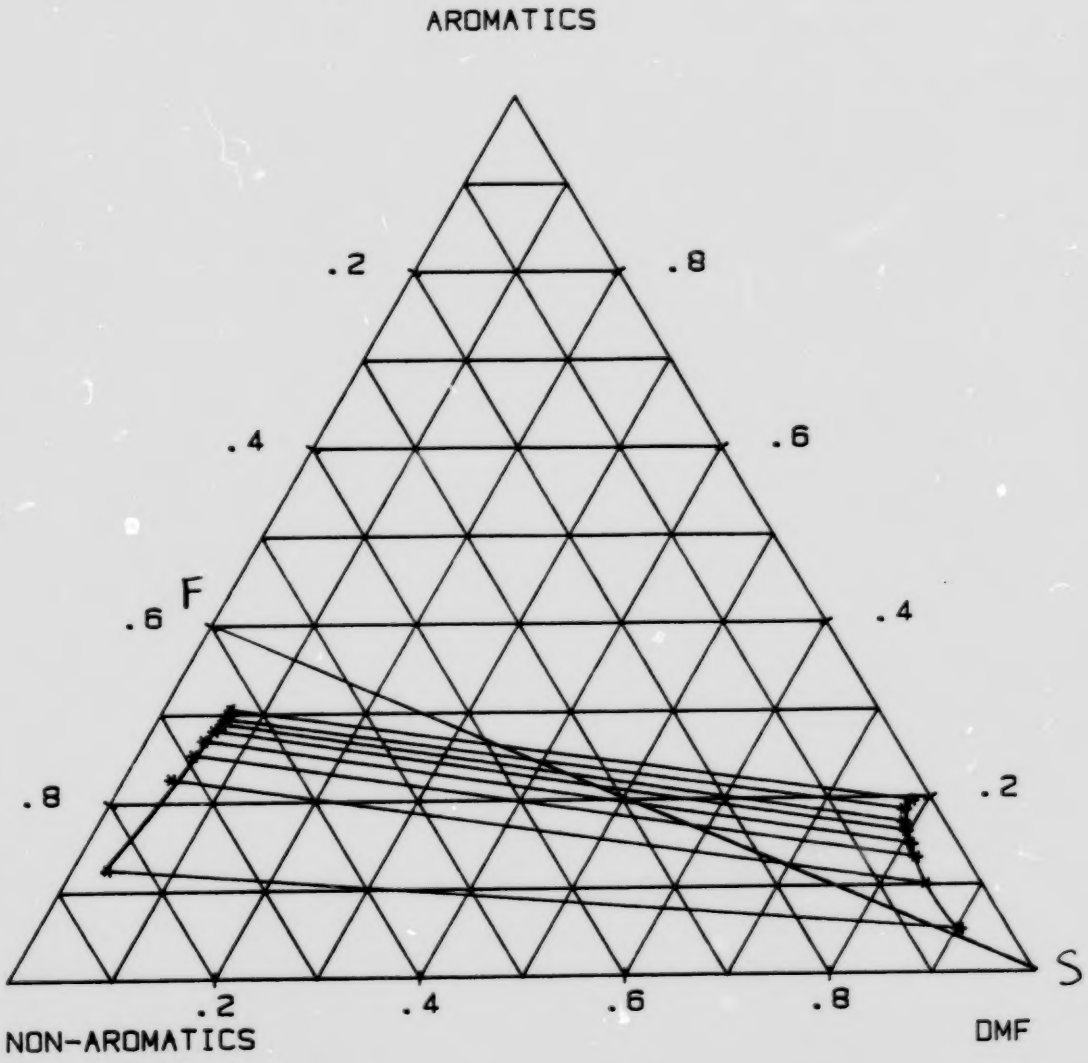
F = Feed
S = Solvent



TIELINES FOR DMF EXTRACTION
OF SYNCRUDE MIDDLE DISTILLATE
AT (APPROXIMATELY) 10C

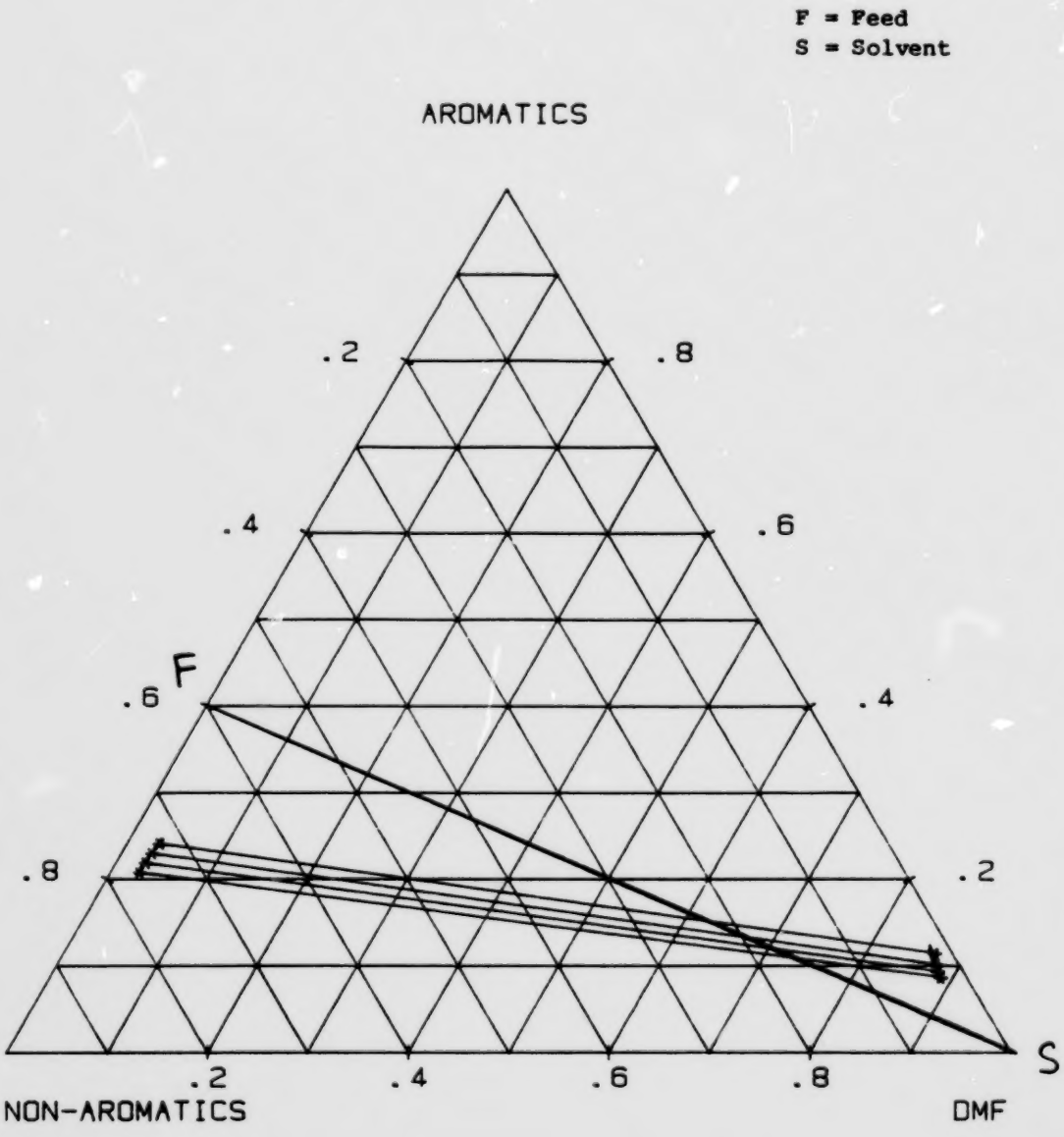
FIGURE 4.16

F = Feed
S = Solvent



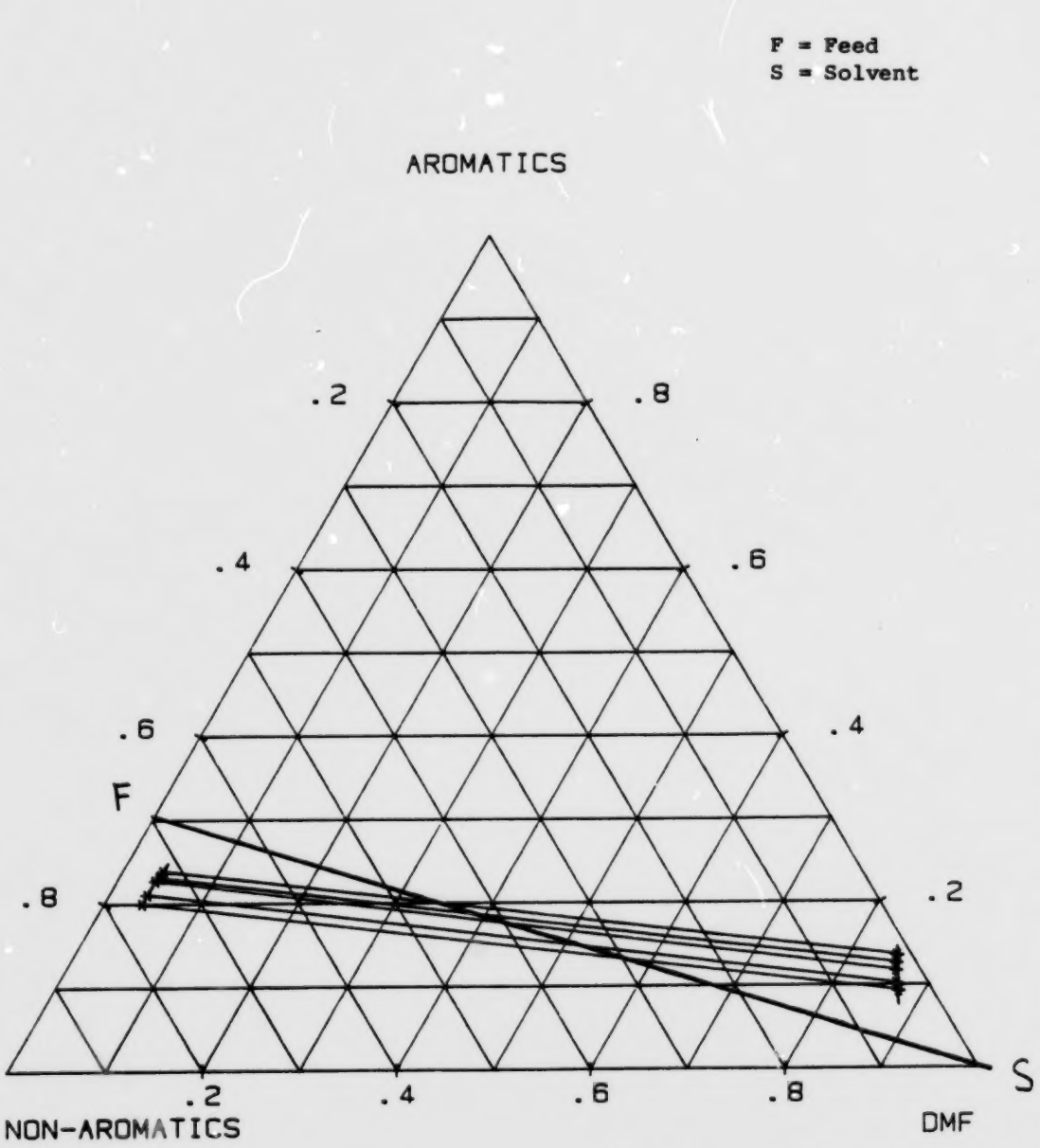
TIELINES FOR DMF EXTRACTION
OF SYNCRUDE MIDDLE DISTILLATE
AT (APPROXIMATELY) 20C

FIGURE 4.17



TIELINES FOR DMF EXTRACTION
OF SUNCOR MIDDLE DISTILLATE
AT (APPROXIMATELY) 0C

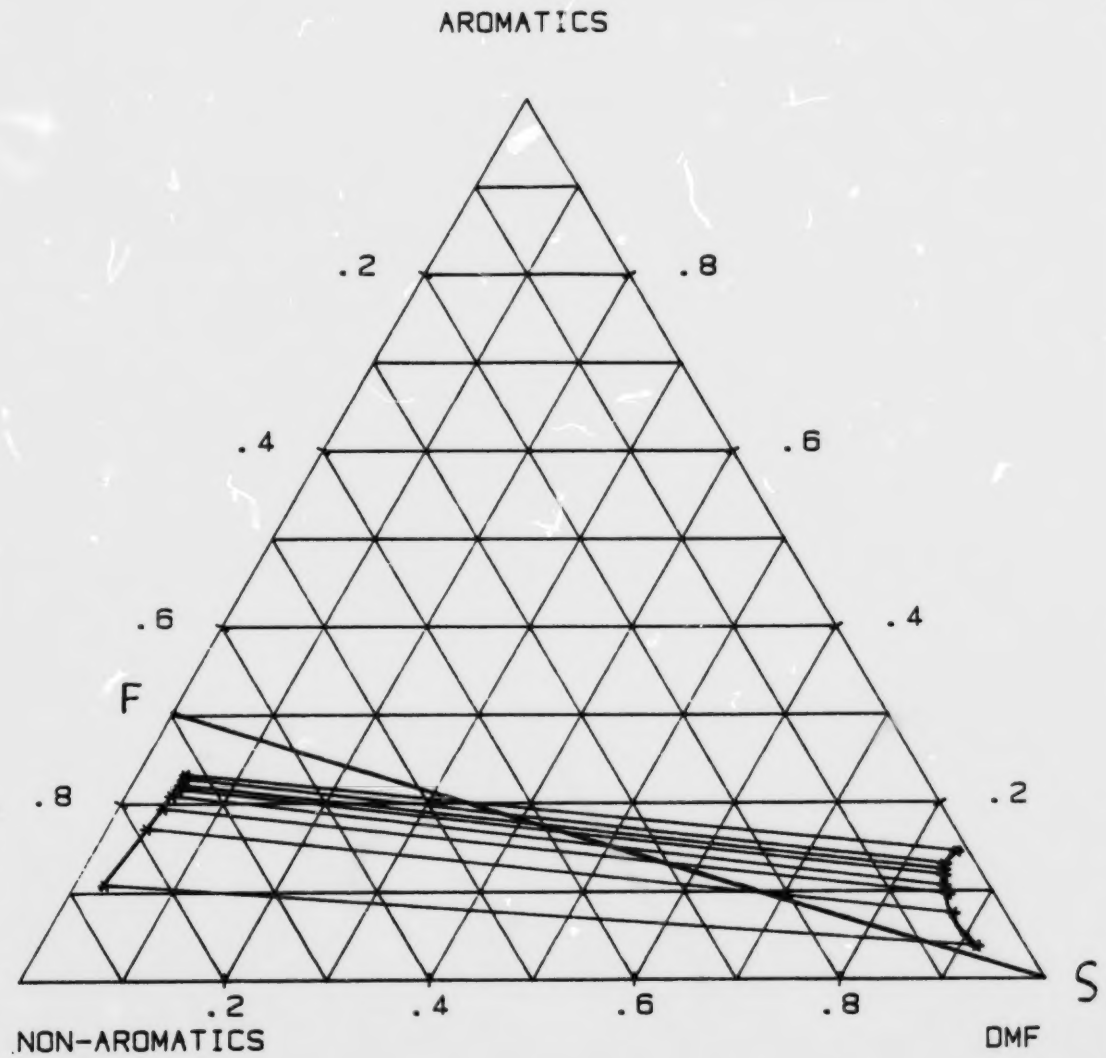
FIGURE 4.18



TIELINES FOR DMF EXTRACTION
OF SUNCOR MIDDLE DISTILLATE
AT (APPROXIMATELY) 10C

FIGURE 4.19

F = Feed
S = Solvent



TIELINES FOR DMF EXTRACTION
OF SUNCOR MIDDLE DISTILLATE
AT (APPROXIMATELY) 20C

FIGURE 4.20

Phase Diagram for the Acetonitrile-
Octyltoluene-n-Tetradecane System (9)

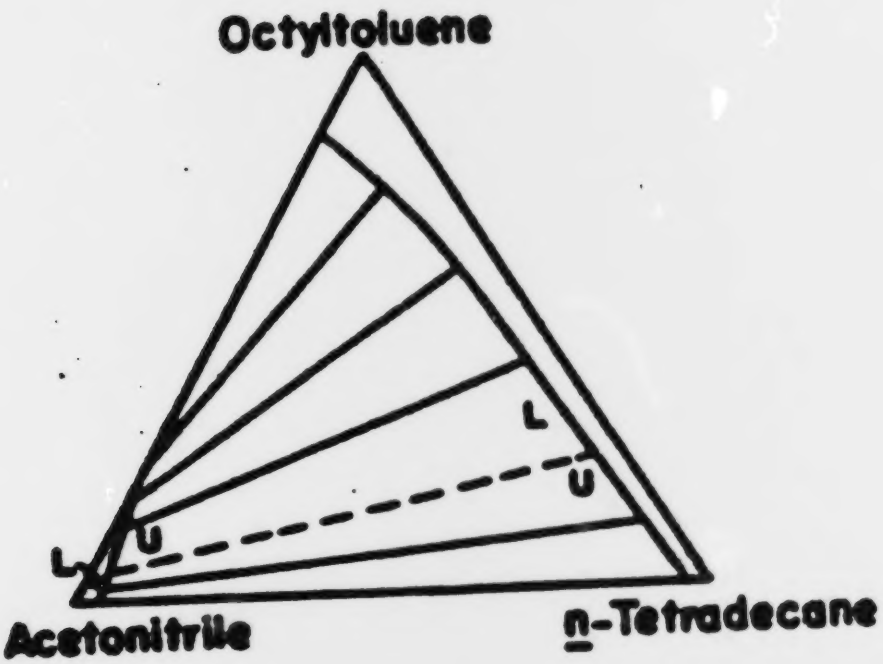
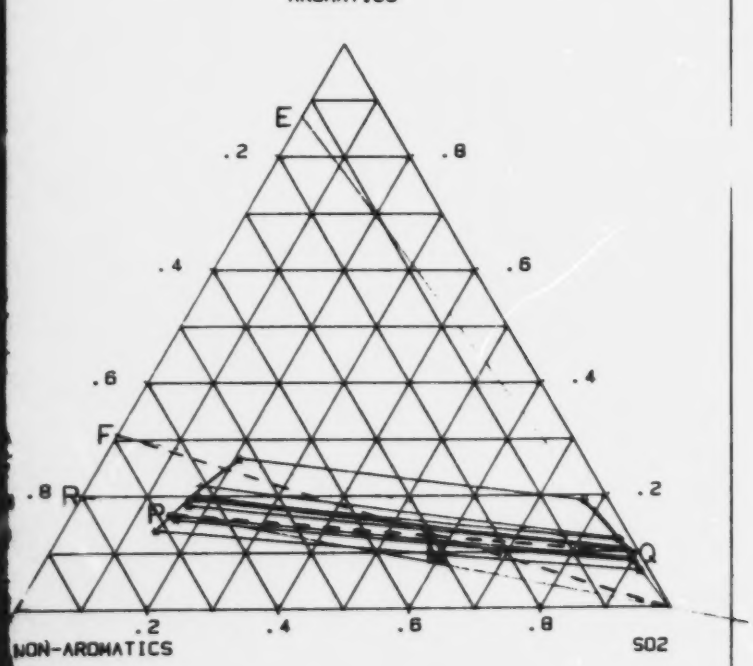


FIGURE 4.21

Process Design for SO_2 Extraction of Suncor Middle Distillate at -12°C

Estimated maximum aromatics content of extract: 87-90 wt.%.
Target aromatics content of raffinate: 20 wt.%.
Solvent/oil ratio: 1.375 wt/wt.
Number of theoretical plates required: Between 1 and 2 (closer to 1 than 2).



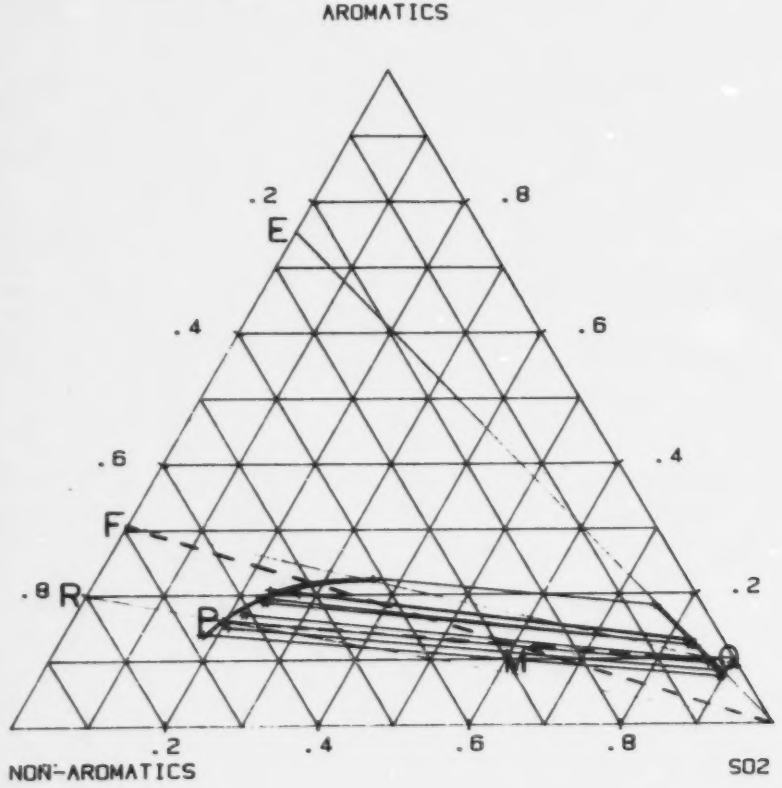
TIE-LINES FOR SO2 EXTRACTION OF SYNCRUDE AND SUNCOR MIDDLE DISTILLATES AT (APPROXIMATELY) -12C

E = Extract
F = Feed
M = Operating point
H = Feed + Solvent
P = Raffinate phase
Q = Extract phase
R = Raffinate
+—+ = Syncrude tie-lines
∗—∗ = Suncor tie-lines

FIGURE 4.22

Process Design for SO_2 Extraction of Suncor Middle Distillate at 2°C

Estimated maximum aromatics content of extract: 75 wt.%.
Target aromatics content of raffinate: 20 wt.%.
Solvent/oil ratio: 1.7 wt/wt.
Number of theoretical plates required: Slightly over 1.



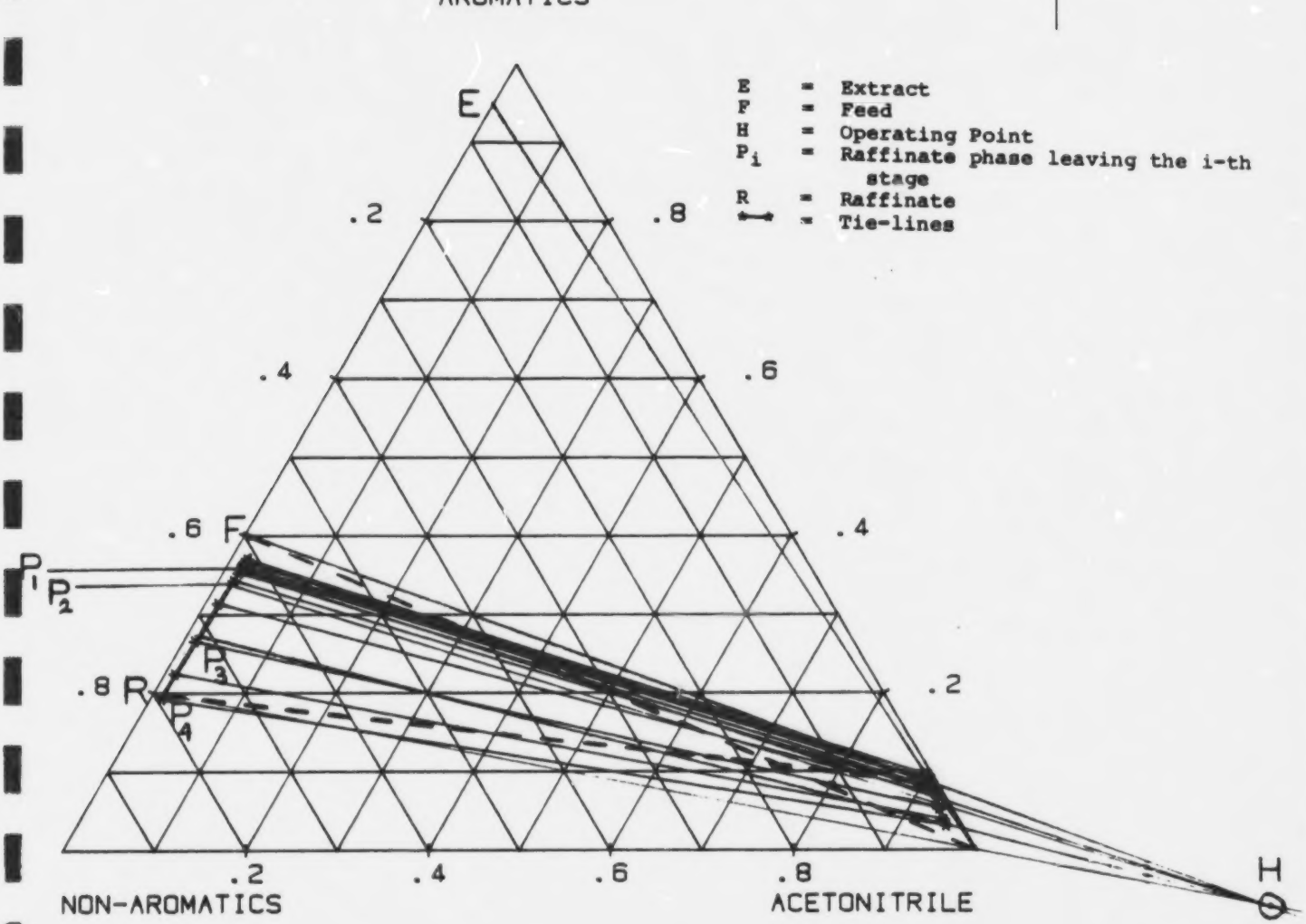
E = Extract
F = Feed
H = Operating point
M = Feed + Solvent
P = Raffinate phase
Q = Extract phase
R = Raffinate
⟷ = Syncrude tie-lines
⟷ = Suncor tie-lines

TIE-LINES FOR SO2 EXTRACTION OF
SYNCRUDE AND SUNCOR MIDDLE DISTILLATES
AT (APPROXIMATELY) 2C

FIGURE 4.23

Process Design for Syncrude Middle Distillate Extraction with Acetonitrile at 0°C

Extract aromatics content:	95 wt.%
Raffinate aromatics content:	20 wt.%
Solvent/Oil ratio:	2.7 wt/wt
Number of theoretical plates required:	4+

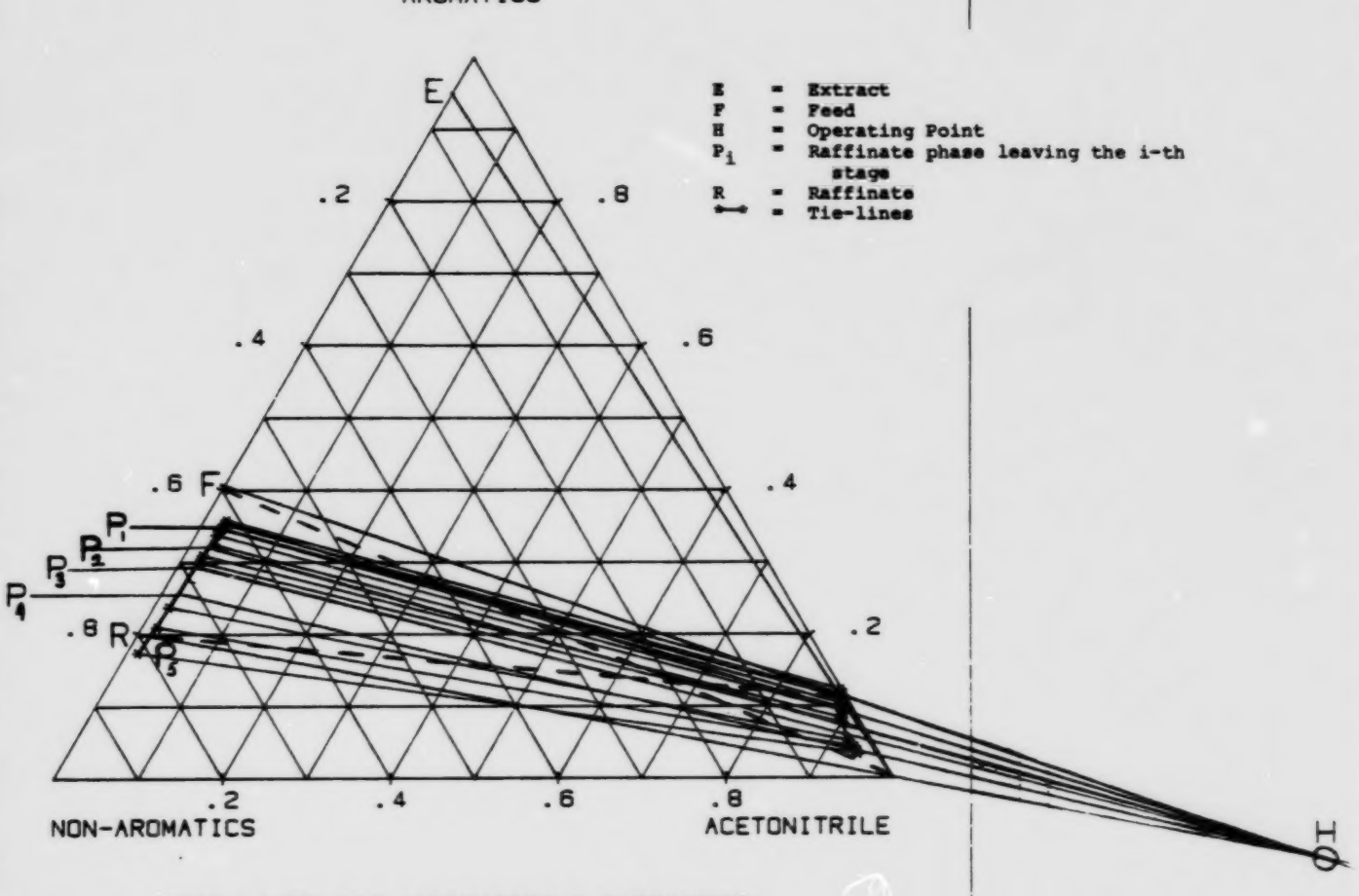


TIE-LINES FOR ACETONITRILE EXTRACTION
OF SYNCRUDE MIDDLE DISTILLATE
AT (APPROXIMATELY) 0C

FIGURE 4.24

Process Design for Syncrude Middle Distillate Extraction with Acetonitrile at 20°C

Extract aromatics content:	95 wt.%
Raffinate aromatics content:	20 wt.%
Solvent/Oil ratio:	2.0 wt/wt
Number of theoretical plates required:	5



TIE-LINES FOR ACETONITRILE EXTRACTION
OF SYNCRUDE MIDDLE DISTILLATE
AT (APPROXIMATELY) 20C

FIGURE 4.25

Process Design for Suncor
Middle Distillate Extraction with
Acetonitrile at 0°C

Extract aromatics content:	95 wt.%
Raffinate aromatics content:	20 wt.%
Solvent/Oil ratio:	1.9 wt/wt
Number of theoretical plates required:	3-4

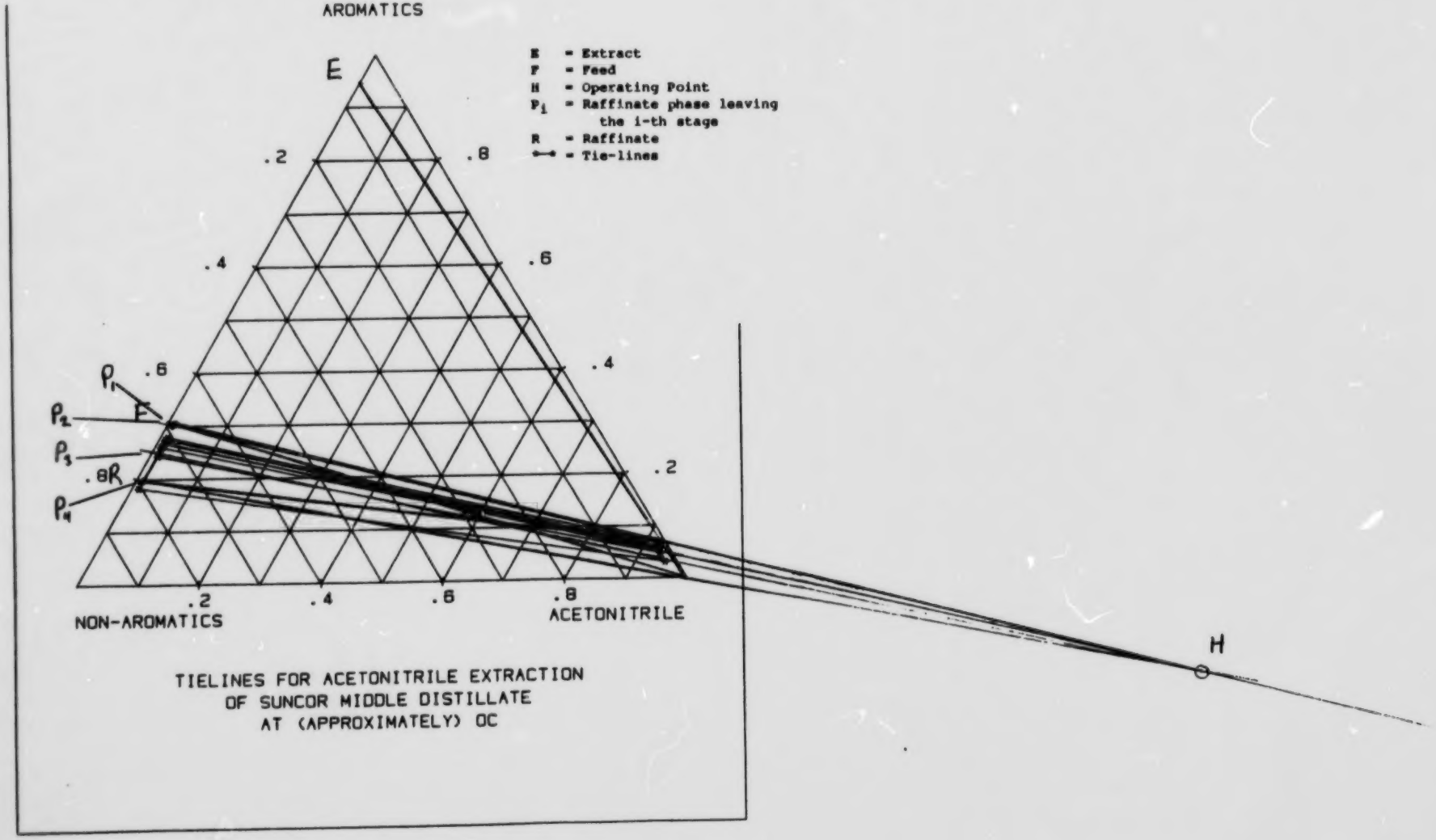
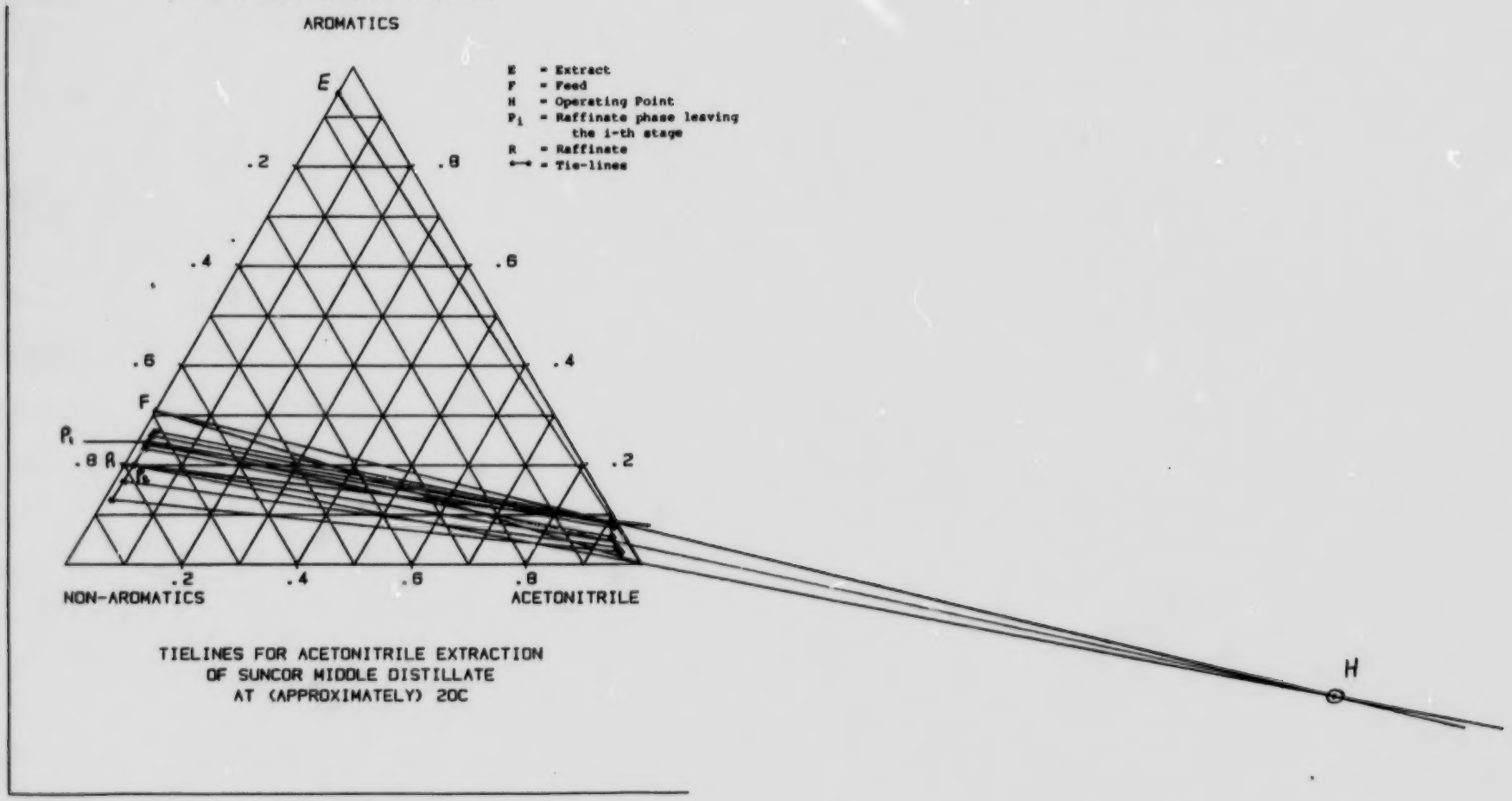


FIGURE 4.26

Process Design for Suncor
Middle Distillate Extraction with
Acetonitrile at 20°C

Extract aromatics content:	95 wt.%
Raffinate aromatics content:	20 wt.%
Solvent/Oil ratio:	1.5 wt/wt
Number of theoretical plates required:	2+

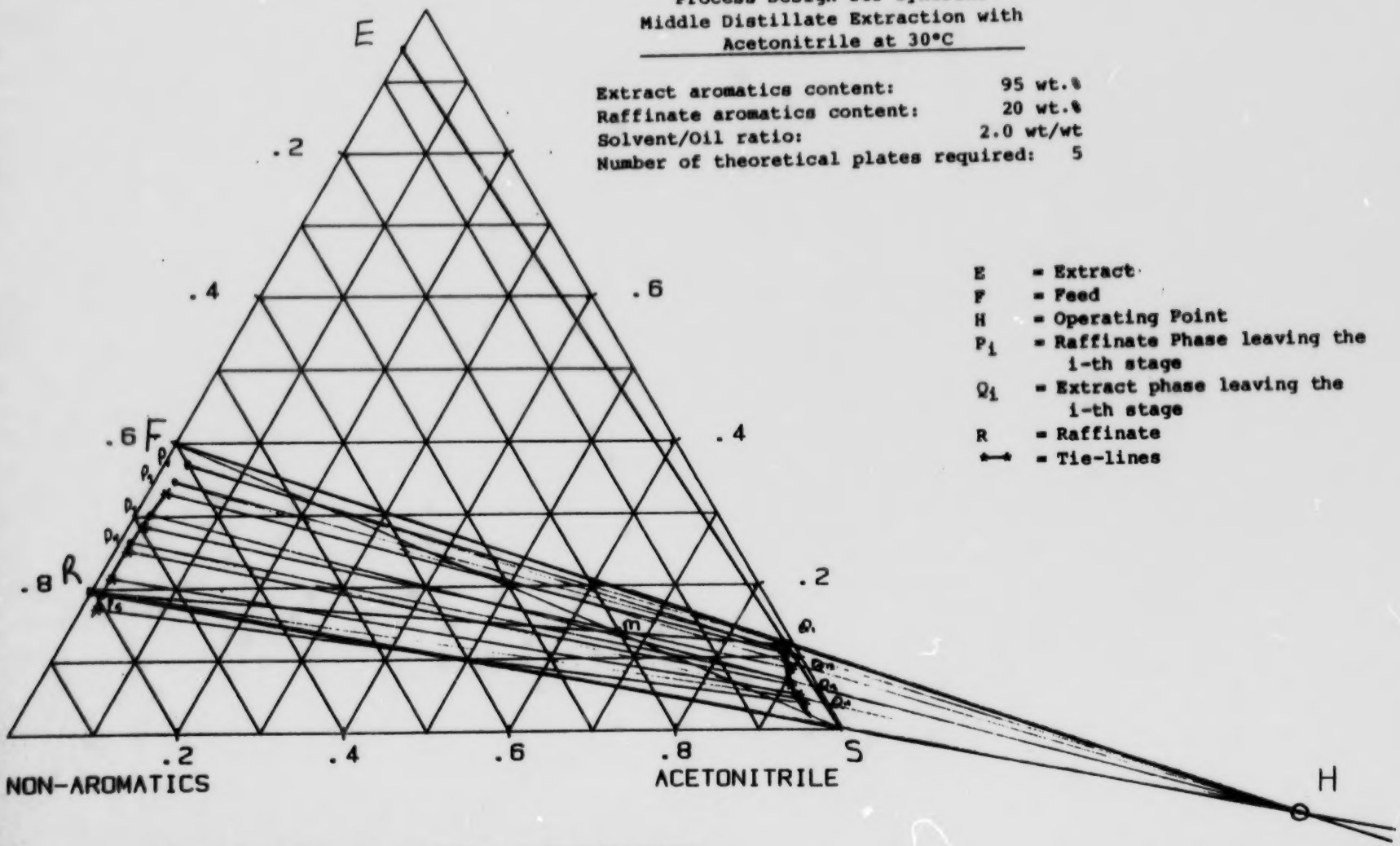


TIELINES FOR ACETONITRILE EXTRACTION
OF SUNCOR MIDDLE DISTILLATE
AT (APPROXIMATELY) 20C

FIGURE 4.27

Process Design for Syncrude
Middle Distillate Extraction with
Acetonitrile at 30°C

Extract aromatics content: 95 wt.%
Raffinate aromatics content: 20 wt.%
Solvent/Oil ratio: 2.0 wt/wt
Number of theoretical plates required: 5



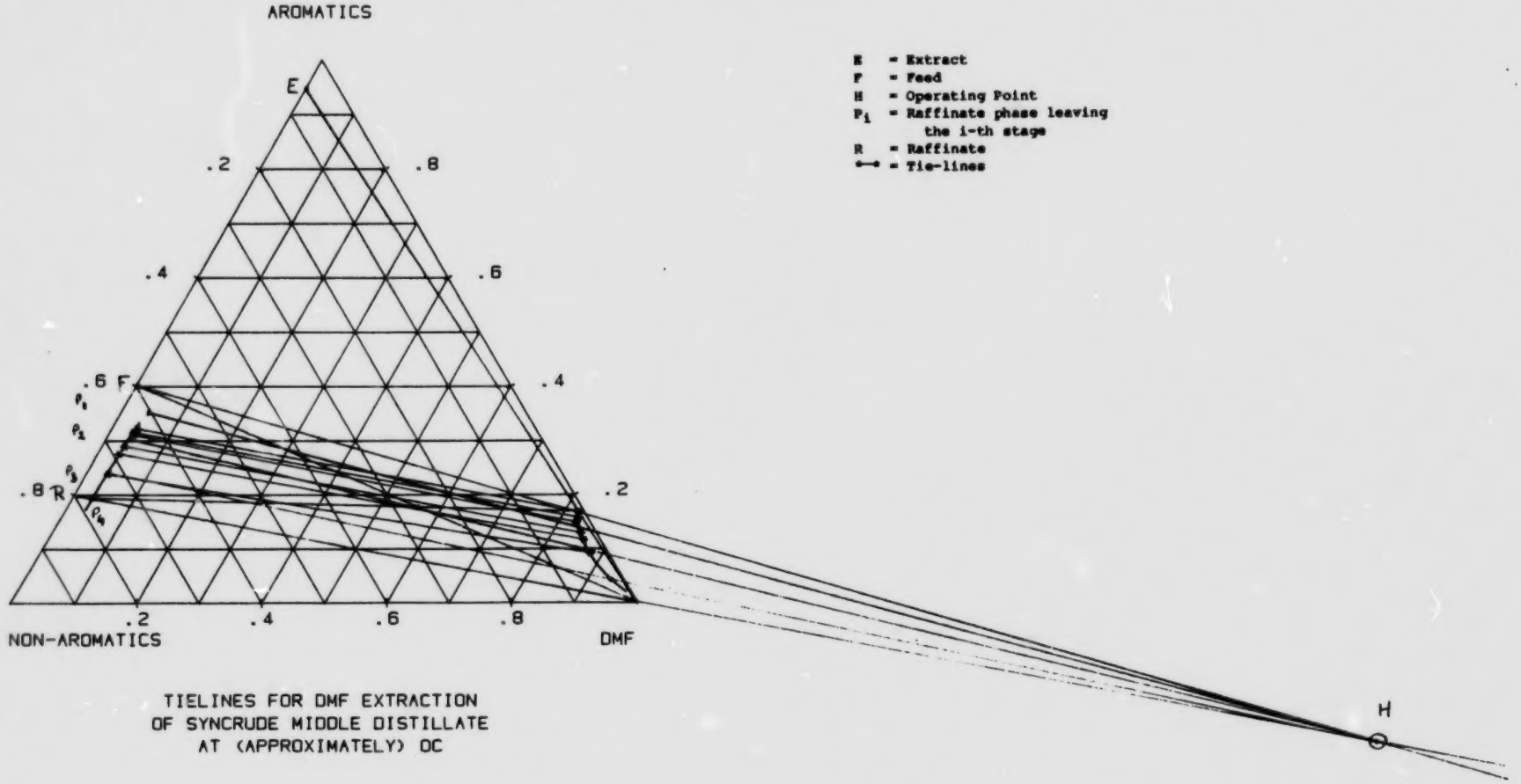
E = Extract
F = Feed
H = Operating Point
P_i = Raffinate Phase leaving the i-th stage
Q_i = Extract phase leaving the i-th stage
R = Raffinate
⟷ = Tie-lines

TIELINES FOR ACETONITRILE EXTRACTION
OF SYNCRUDE MIDDLE DISTILLATE
AT (APPROXIMATELY) 30C

FIGURE 4.28

Process Design for Syncrude Middle Distillate Extraction with Dimethyl Formamide at 0°C

Extract aromatics content: 95 wt.%
Raffinate aromatics content: 20 wt.%
Solvent/Oil ratio: 1.4 wt/wt
Number of theoretical plates required: 2.5

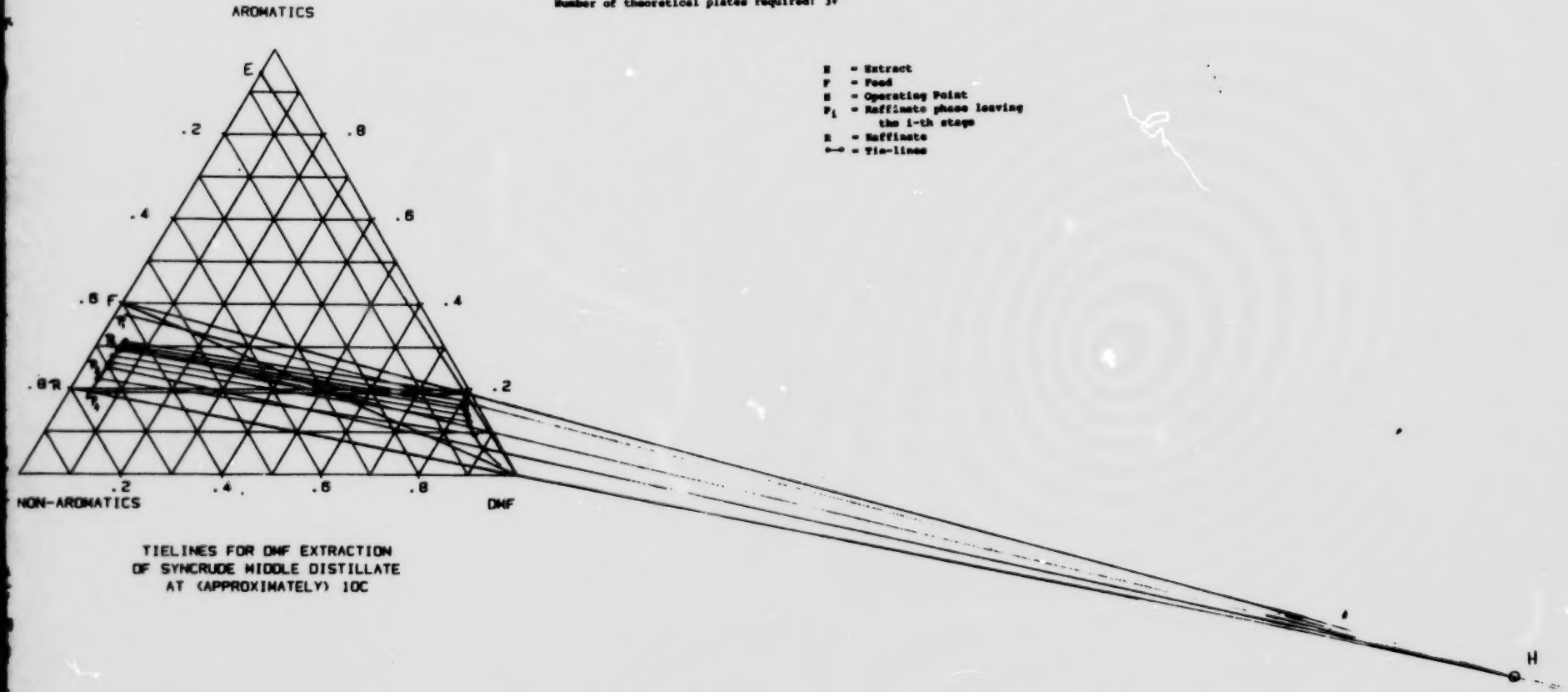


TIELINES FOR DMF EXTRACTION OF SYNCRUDE MIDDLE DISTILLATE AT (APPROXIMATELY) OC

FIGURE 4.29

Process Design for Syncrude Middle Distillate Extraction with Dimethyl Formamide at 10°C

Extract aromatics content:	95 wt.%
Raffinate aromatics content:	20 wt.%
Solvent/Oil ratio:	1.1 wt/wt
Number of theoretical plates required:	3+

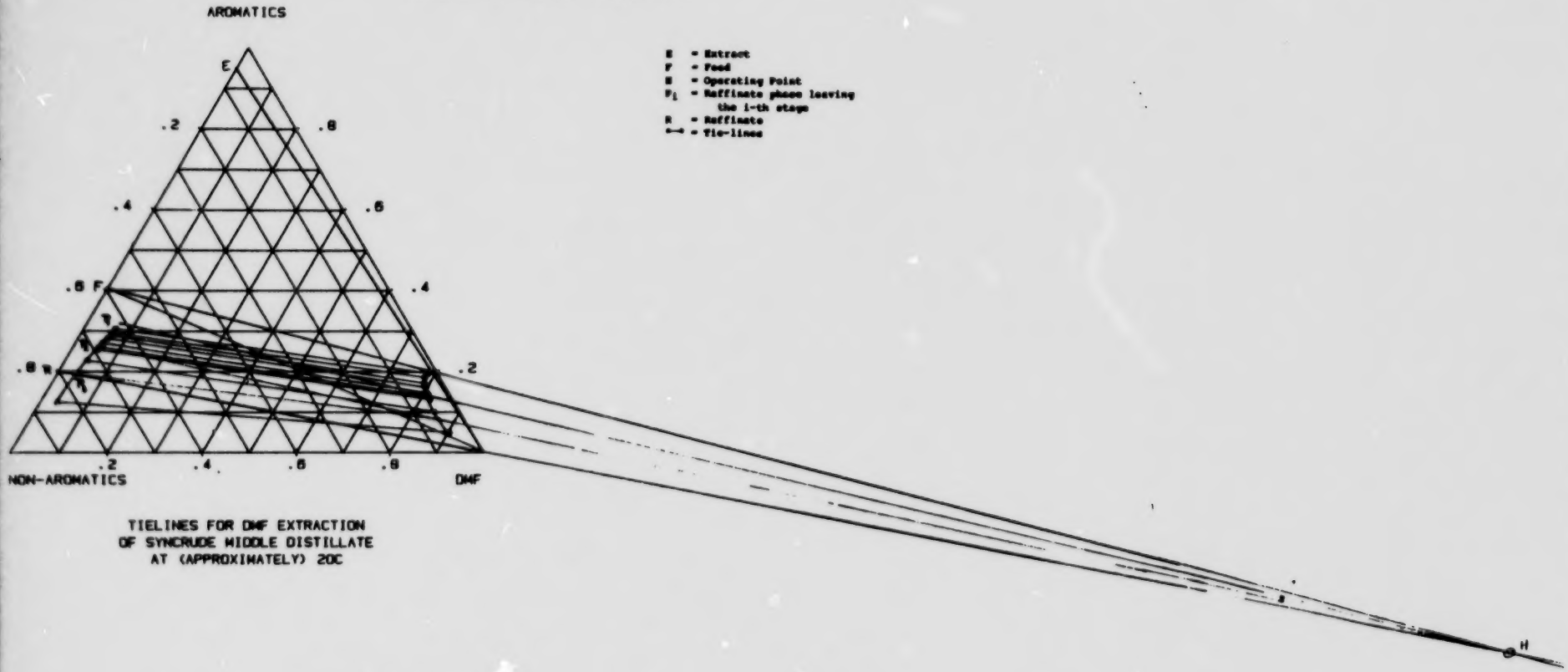


TIELINES FOR DMF EXTRACTION
OF SYNCRUDE MIDDLE DISTILLATE
AT (APPROXIMATELY) 10C

FIGURE 4.30

Process Design for Syncrude Middle Distillate Extraction with Dimethyl Formamide at 20°C

Extract aromatics content:	95 wt.%
Raffinate aromatics content:	20 wt.%
Solvent/Oil ratio:	1.1 wt/wt
Number of theoretical plates required:	2-3



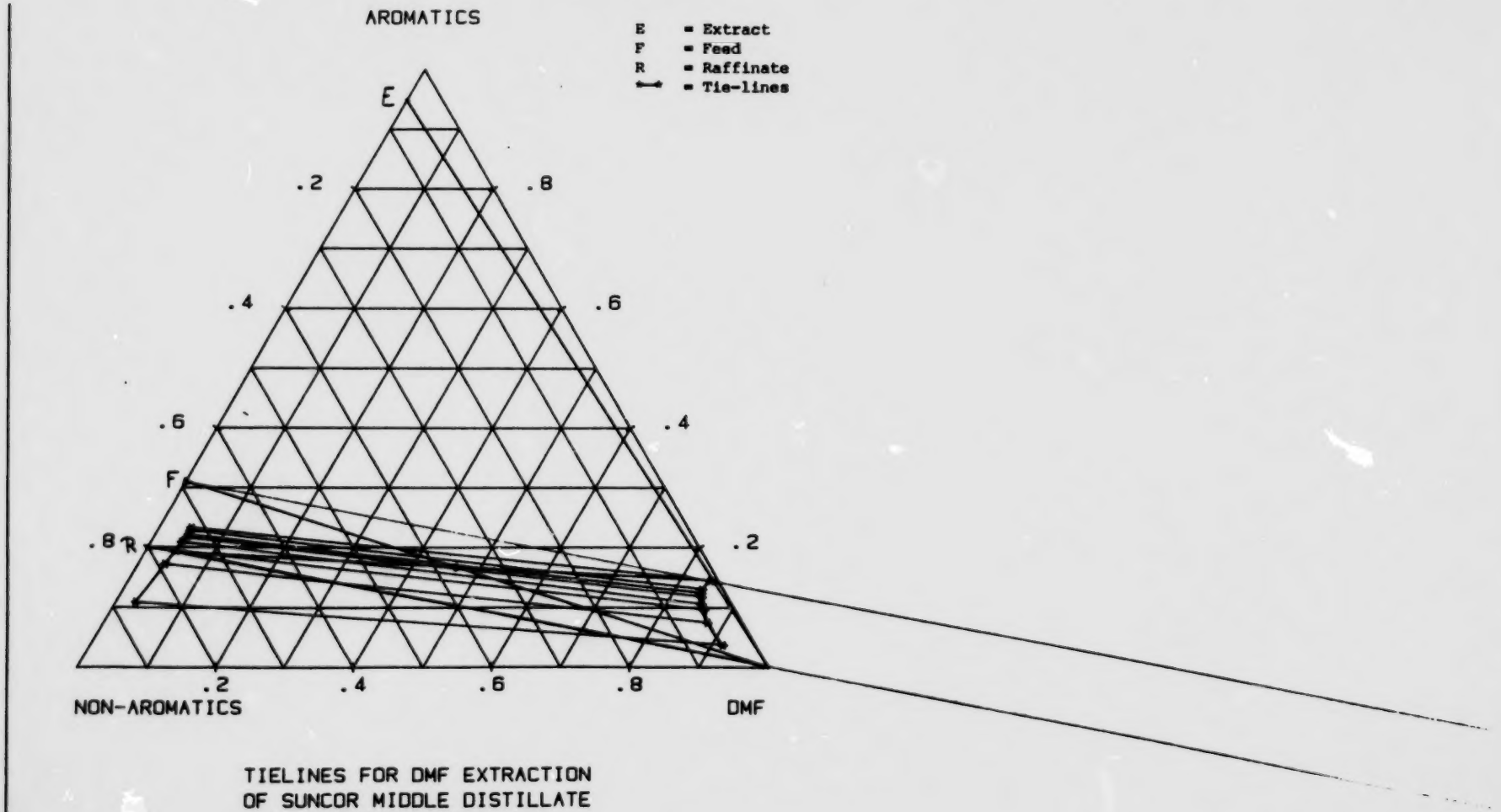
TIELINES FOR DMF EXTRACTION OF SYNCRUDE MIDDLE DISTILLATE AT (APPROXIMATELY) 20C

FIGURE 4.51

Process Design for Suncor
Middle Distillate Extraction with
Dimethyl Formamide at 20°C

Extract aromatics content: 95 wt.%
Raffinate aromatics content: 20 wt.%

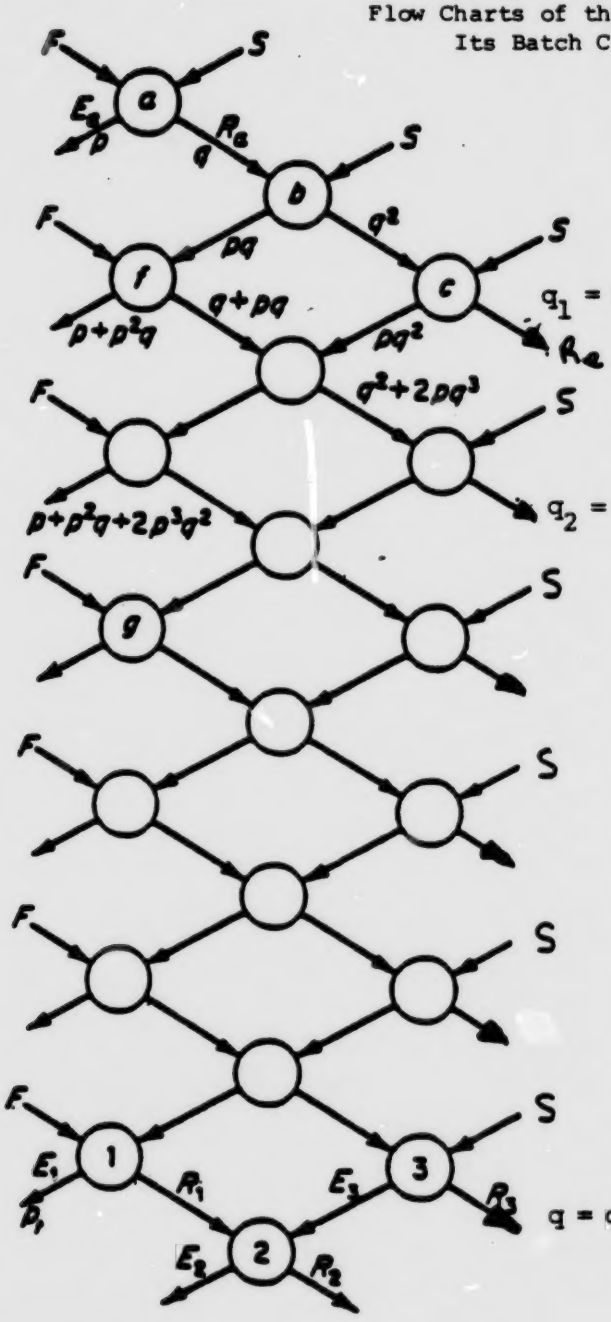
Operating lines diverge - extraction not possible at these conditions



TIELINES FOR DMF EXTRACTION
OF SUNCOR MIDDLE DISTILLATE
AT (APPROXIMATELY) 20C

FIGURE 4.32

Batch Simulation of Three-Stage Continuous Countercurrent Extraction with Acetonitrile at 20°C, Syncrude Middle Distillate Feed Flow Charts of the Continuous Process and Its Batch Cascade Simulation



$q_1 = q^3$, $t = 1$

$q_2 = q^3(1+2pq)$, $t = 2$

$q = q^3[1+2pq+\ldots \quad \gamma_t (pq)^{t-1}]$, $t = t$

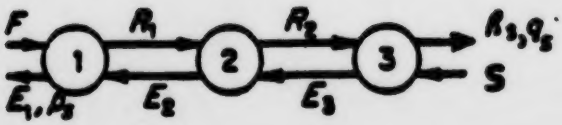
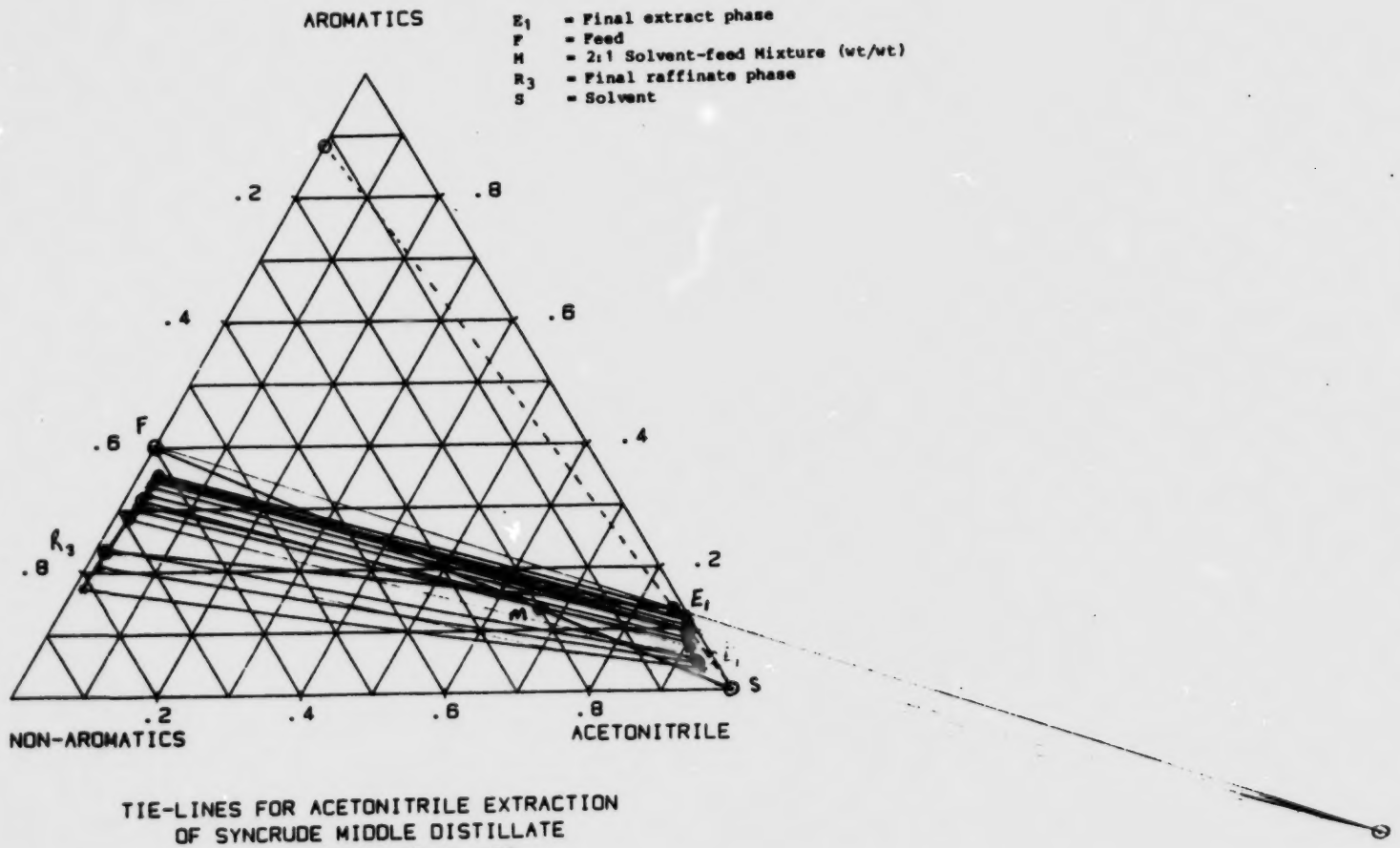


FIGURE 4.33

Evaluation of the Batch Simulation of
Three-Stage Countercurrent Extraction



TIE-LINES FOR ACETONITRILE EXTRACTION
OF SYNCRUDE MIDDLE DISTILLATE
AT (APPROXIMATELY) 20C

FIGURE 4.34

Pilot Plant Extractions of Syncrude
Middle Distillate with Acetonitrile at
20°C; Runs 20-4, 20-9 and 20-23
Raffinate and Extract Phase Compositions

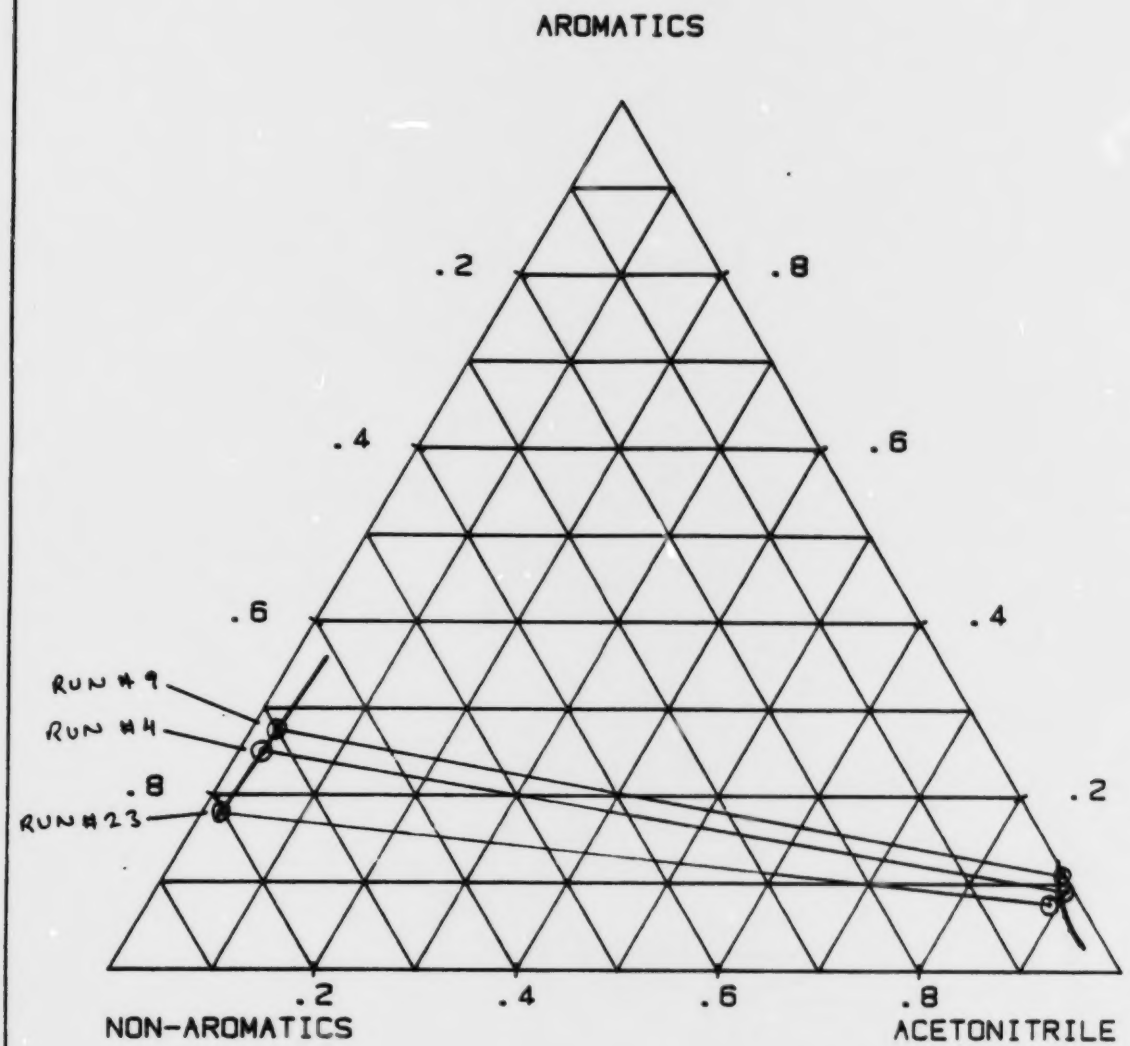


FIGURE 4.35

Pilot Plant Extractions of Syncrude
Middle Distillate with Acetonitrile at
30°C; Runs 20-12 and 20-14
Raffinate and Extract Phase Compositions

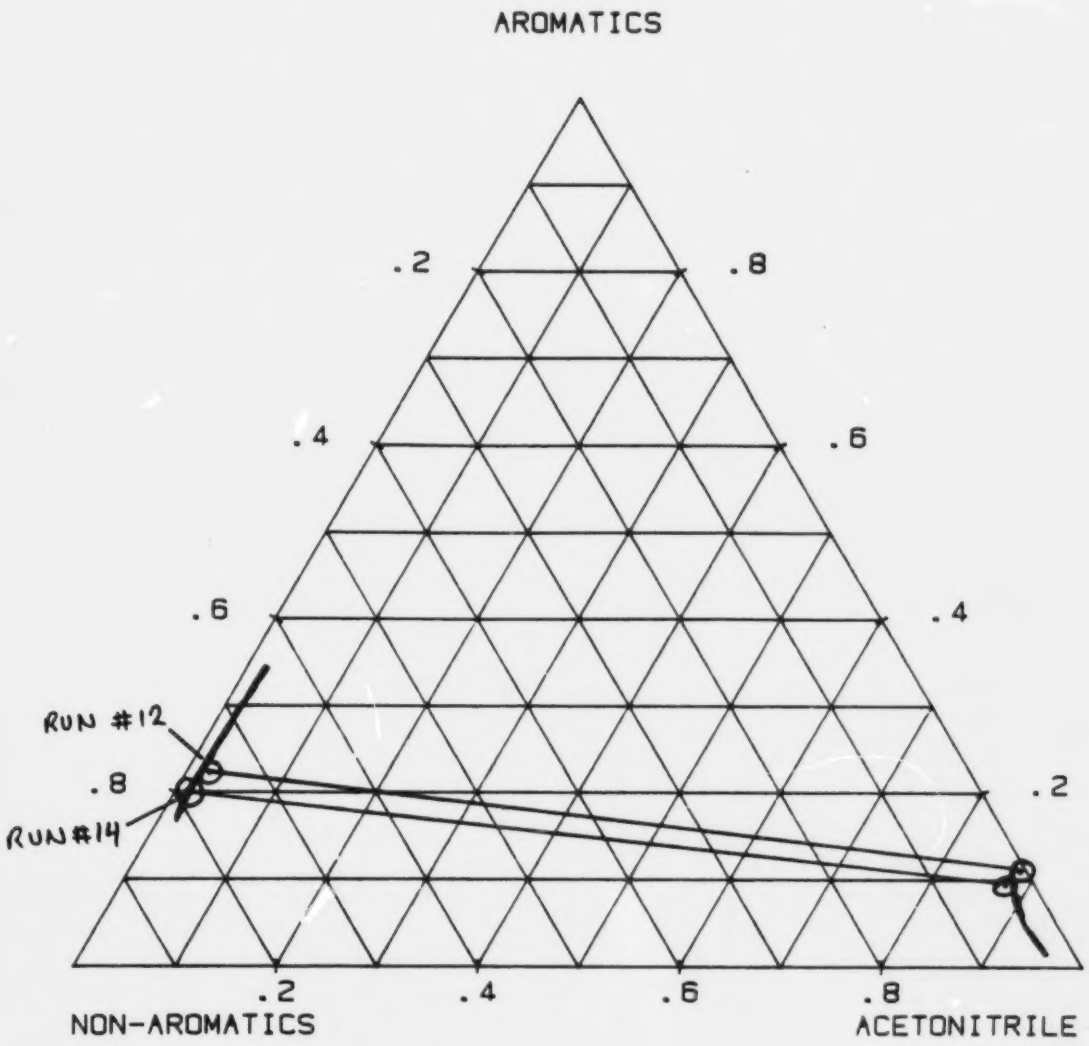


FIGURE 4.36

Pilot Plant Extractions of Suncor
Middle Distillate with Acetonitrile at
20°C; Runs 20-17, 20-19 and 20-22
Raffinate and Extract Phase Compositions

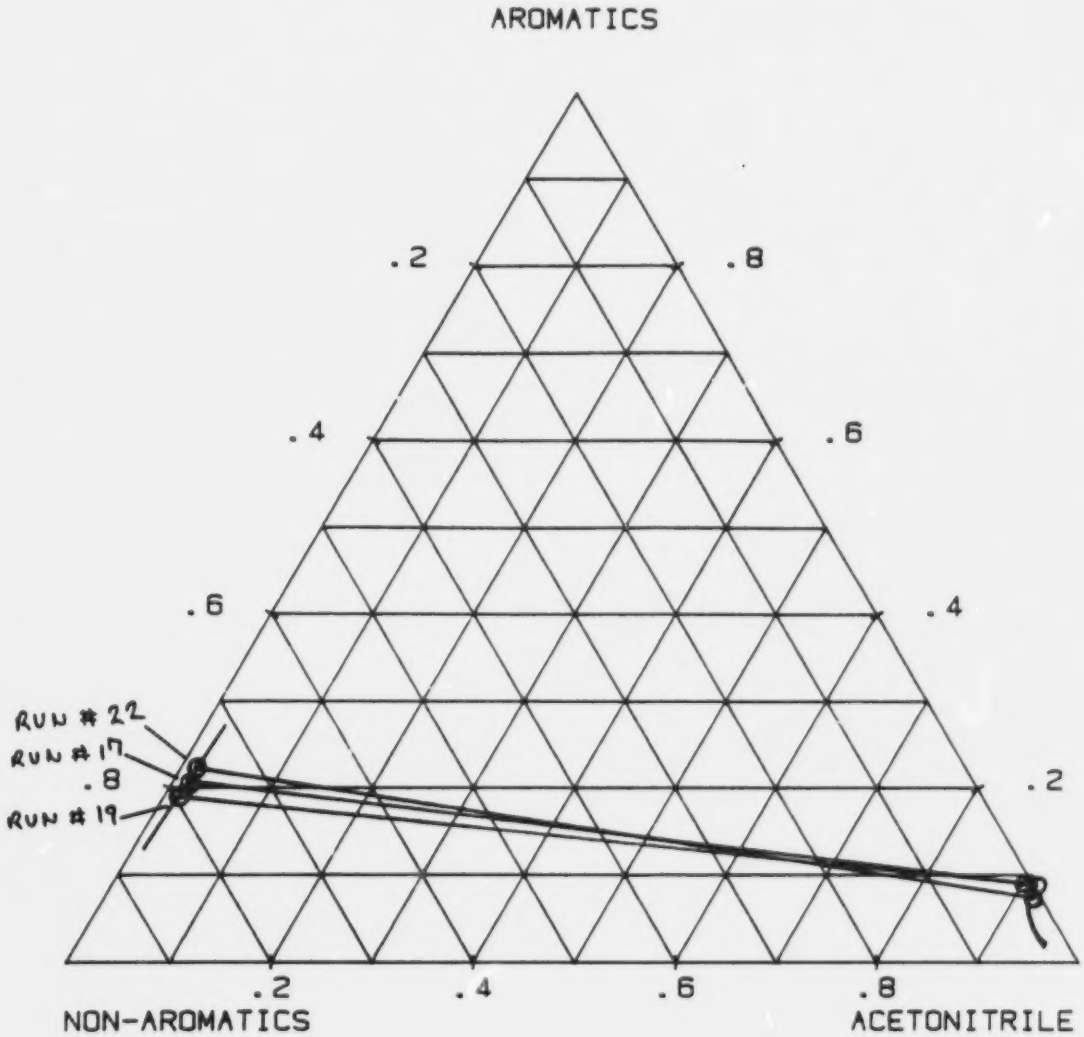
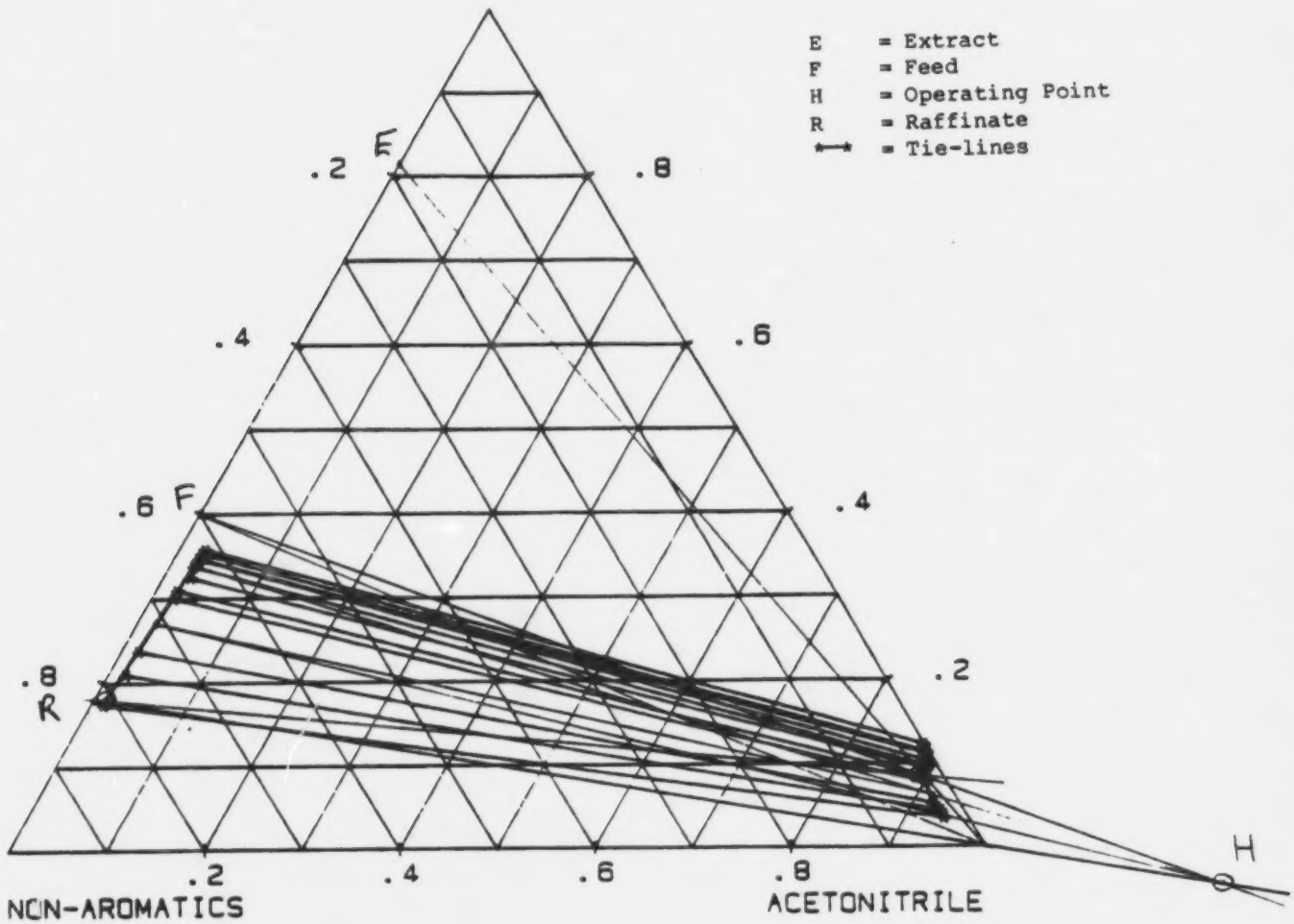


FIGURE 4.37

Process Design for Syncrude
Middle Distillate Extraction with
Acetonitrile at 20°C

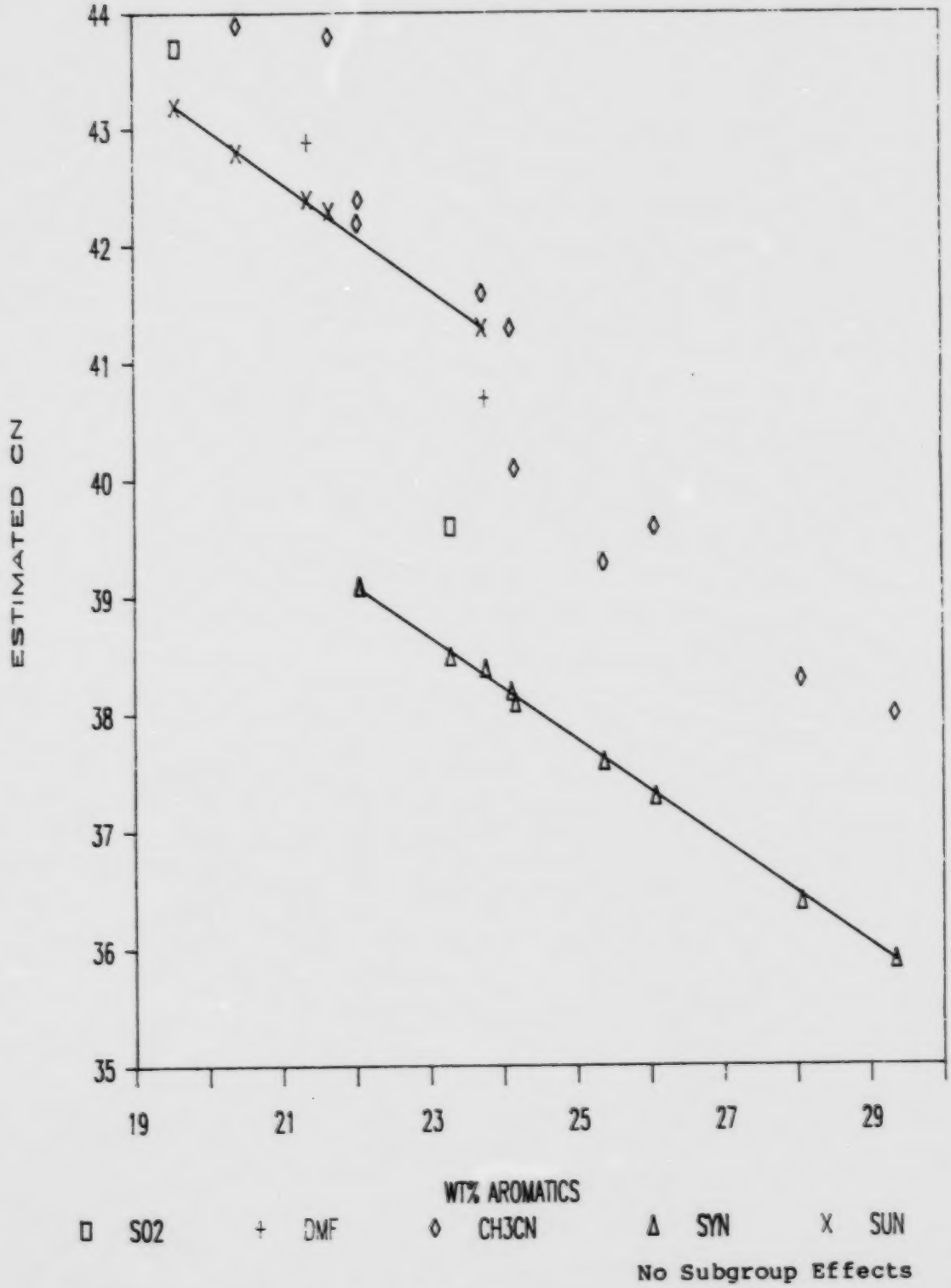
Extract aromatics content: 82 wt.%
Raffinate aromatics content: 17 wt.%
Solvent/Oil ratio: 3:1 wt/wt
Number of theoretical plates required: 2.5



TIE-LINES FOR ACETONITRILE EXTRACTION
OF SYNCRUDE MIDDLE DISTILLATE
AT (APPROXIMATELY) 20C

FIGURE 4.38

Cetane Number Enhancement
Due to Subgroup Selectivity -
Comparison of Solvents



No Subgroup Effects

FIGURE 4.39

Cetane Number Enhancement
Due to Subgroup Selectivity -
Comparison of Syncrude and
Suncor Raffinates

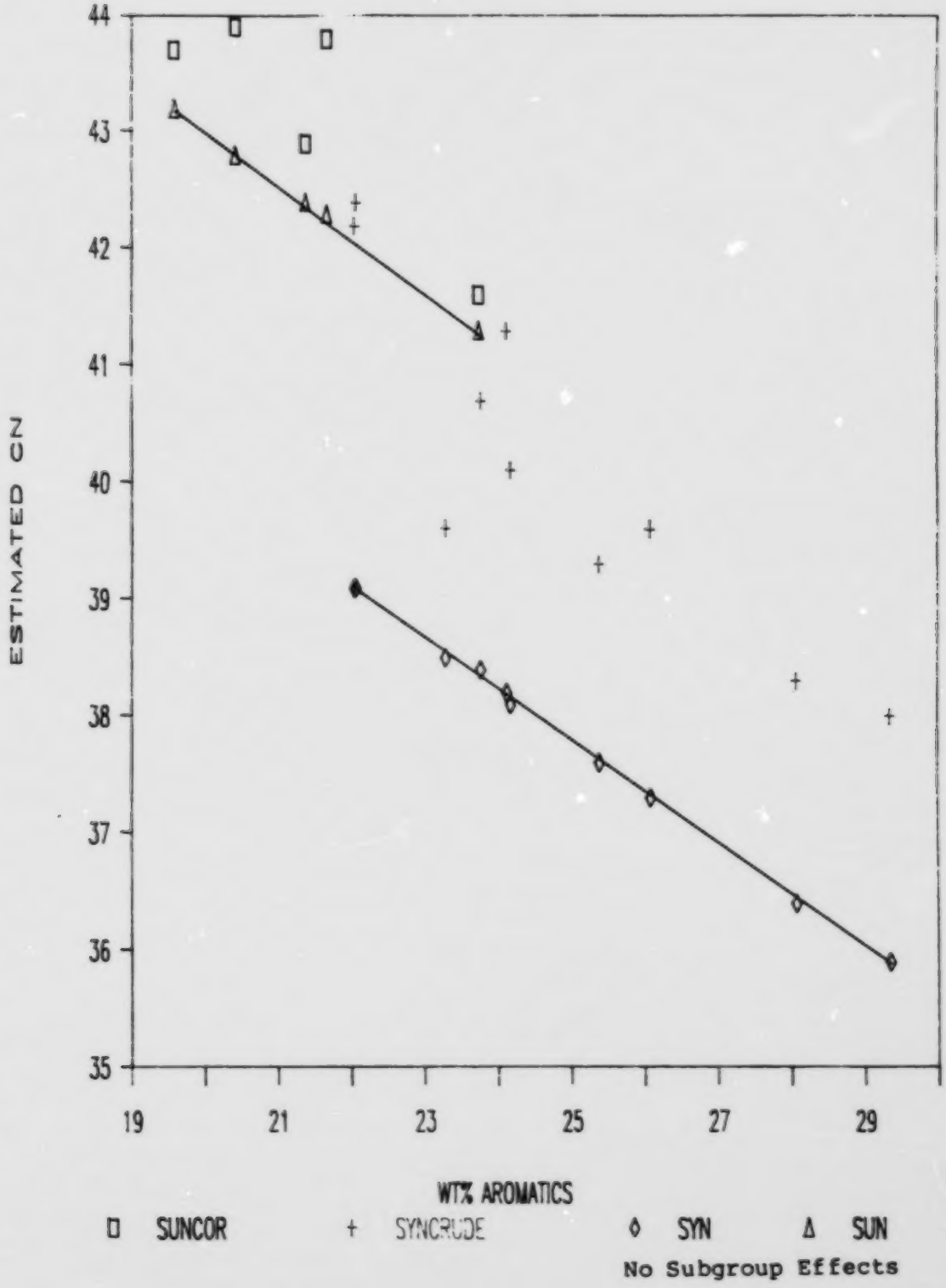
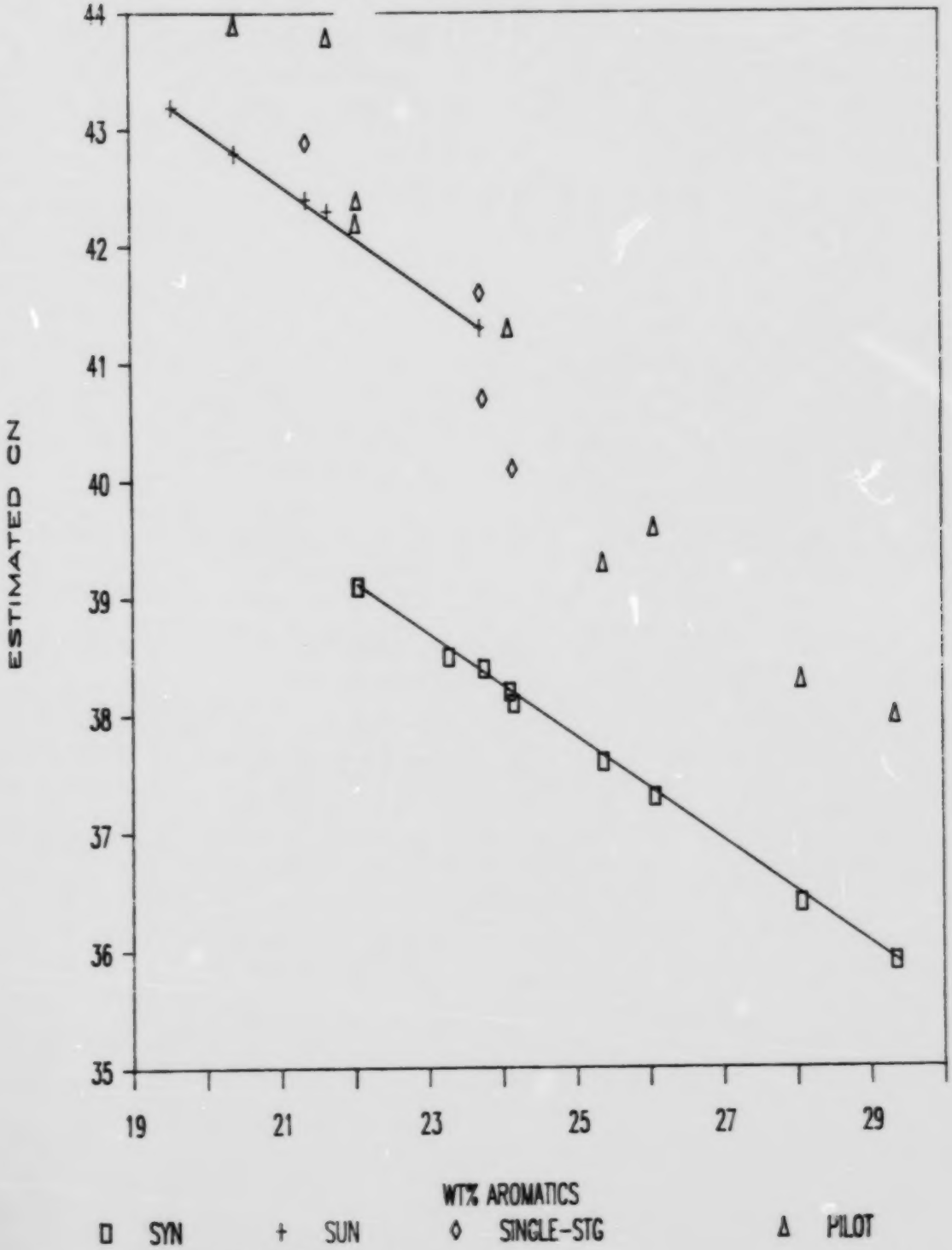


FIGURE 4.40

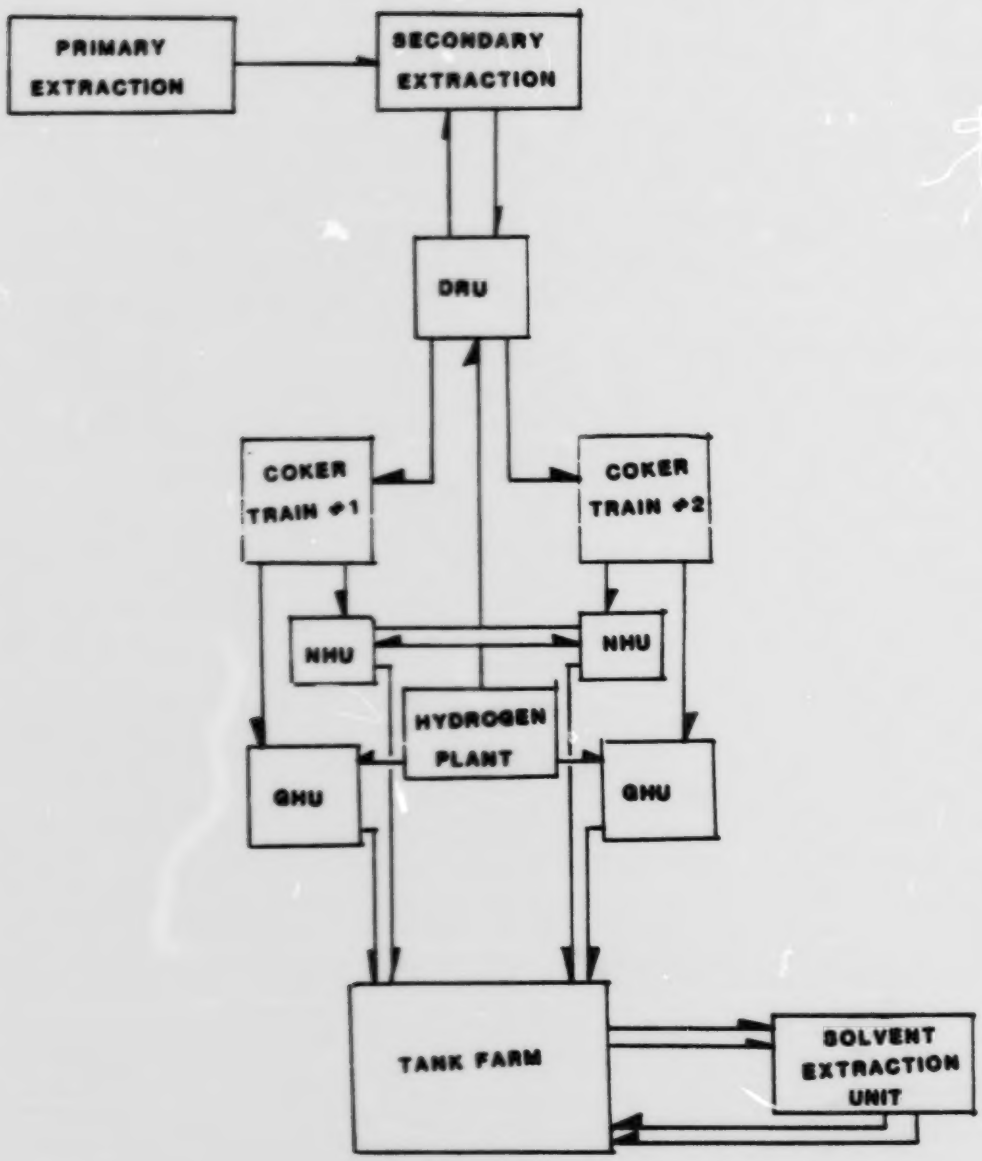
Cetane Number Enhancement
Due to Subgroup Selectivity -
Comparison of Single-Stage
and Pilot Plant Extractions
(Acetonitrile and Dimethyl
Formamide Solvents)



No Subgroup Effects

FIGURE 4.41

SYNCRUDE OPERATION OVERVIEW



DRU = Diluent-Recovery Unit
NHU = Naphtha Hydrogenation Unit
GHU = Gas Oil Hydrogenation Unit

PROPOSED SOLVENT EXTRACTION UNIT

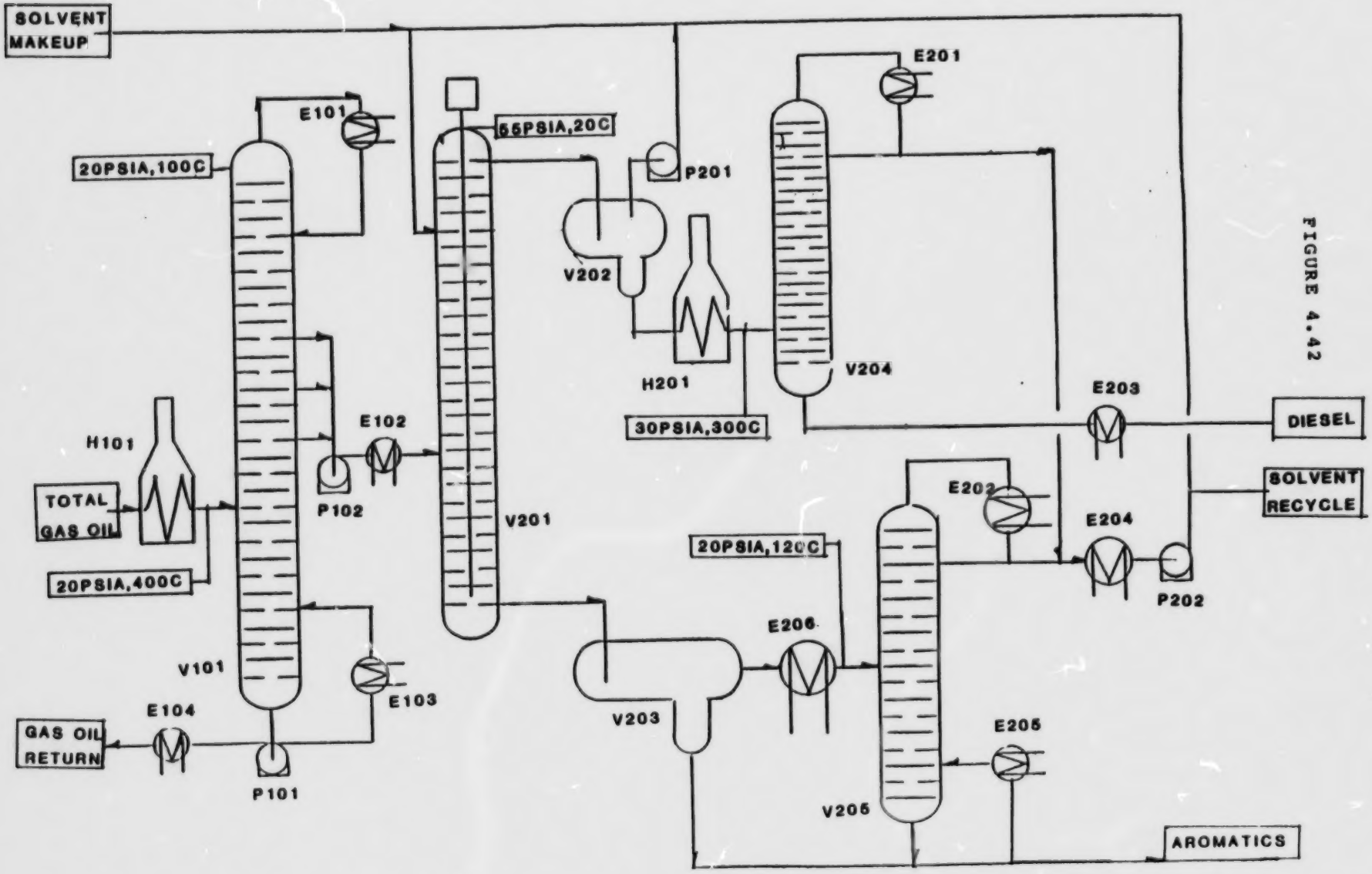


FIGURE 4.42

APPENDIX I

OPERATING MANUAL
PILOT PLANT EXTRACTION UNIT

B.B. Galvez

October, 1985

PETRO-CANADA, INC
RESEARCH AND DEVELOPMENT DEPARTMENT
SHERIDAN PARK, ONTARIO

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1. SAFETY PRECAUTIONS

Extracting Solvent: Acetonitrile (CH_3CN)
(Methyl Cyanide or Cyanomethane)

The following properties and hazard potentials should be considered when handling CH_3CN:

Properties:

M.W.	41.05
Sp. Gr.	0.78
B.P.	81.6°C (178.9°F)
M.P.	-41.9°C

Colorless liquid with aromatic odor; violently reactive; freely miscible with water, alcohol, acetone, chloroform, carbontetrachloride.

Hazardous Potentials:

A). Flammability

Flammable; flash point 5.6°C (42.1°F) Open Cup, 12.8°C (55.0°F) Closed Cup; Ignition temperature 524°C (975.2°F), Vapour density 1.42; Explosive range 4.4-16.0% at 120°C (248°F) and at lower temperature in the presence of Alkali decomposes with evolution of hydrogen cyanide gas.

B) Toxicity:

TLV:	40 ppm	
TDL:	ORL-RAT LD50:	200 mg/kg
IHL:	RAT LCLO:	8000 ppm/4H
SCU-MUS LDLO:		700 mg/kg

Symptoms: Acute headache, dizziness, respiration increase, rapid pulse, nausea; vomiting, unconscious, convulsion, fatal.

Chronic: Headache, lack of appetite, dizziness, weakness, redness of skin, redness with swelling, swelling of H_2O under the skin.

Handling and Storage

Protect containers against physical damage, outdoor or detached storage is preferable. Separate from any source of ignition and combustible materials. Storage room should be well-ventilated. Wear rubber gloves, safety shoes, apron (lab coat).

Emergency Treatment and Measures

A) Hygienic Precautions

Adequate ventilation, no food and smoking in work area. Ear plugs for employees with perforated eardrums. Preclude from exposure those individual with diseases of central nervous system, heart and lungs.

B) Treatment (Follow remedy for cyanides intoxication)

Hydrogen cyanide has a garlicky, oniony and oil of bitter almonds odor.

First aid must be administered immediately. A physician must be called at once.

Inhalation

Walk, carry or drag the victim to fresh air. Have him lie down. Place blankets over his body to maintain body heat.

(1) If victim is conscious and breathing, watch him carefully for asphyxiation; if he lapses into unconsciousness, break an amyl nitrite pearl in a cloth and hold it close to the victim's nose for 15 seconds (the first aider should keep the broken pearls away from his own mouth and nose). Repeat this procedure when there is no response for maximum of only 5 times for 15 seconds at 15 seconds intervals, using a clean cloth and fresh pearl each time. If there is no response at all, medical treatment is required immediately - a nurse may give an intravenous injection of sodium nitrite and sodium thiosulfate.

(2) If the victim is unconscious but breathing, the above (1) described procedure of amyl nitrite inhalation is started immediately. Oxygen should then be administered.

(3) If victim is not breathing, immediately start artificial respiration and continue until breathing starts. Then begin the amyl nitrite inhalations described above. Finally, administer oxygen. In all cases, keep victim quiet and warm until he has fully recovered.

Skin Contact

Immediately deluge the affected area with water from an emergency shower or hose. Walk, carry or drag the victim to fresh air. Remove wet clothing, shoes, and socks. Wash skin thoroughly with water. Have victim lie down and place blankets under and over this body to maintain body heat.

If poisoning occurs as a result of skin contract, apply the First Aid procedure as discussed under "Inhalation".

(C) Fire Precautions

Use dry chemicals, alcohol foam or carbon dioxide. Water spray is ineffective.

Spills and Leakage

a) Absorb with papers. Allow to evaporate on a glass or iron dish in a hood. Dispose by burning the paper.

b) Add excessive sodium hydroxide and calcium hypochlorite solution in a hood. Transfer into a large beaker. After one hour, drain into sewer with sufficient water and wash the split site.

Disposal and Waste Treatment

Add by stirring excessive alcoholic sodium hydroxide. After one hour, evaporate alcohol and add sufficient calcium hypochlorite. Ater 24 hours, drain into sewer with abundant water.

2. THEORY OF LIQUID-LIQUID EXTRACTION PROCESS

Liquid-Liquid extraction often proves to be an economical means of affecting a component separation which would be more difficult using the conventional distillation techniques. Using a selective solvent instead of a gas or vapour phase produces separations comparable to those encounter in vapour-liquid separations.

The reasons for increased interest in liquid-liquid extraction are due to:

(1) Prospects of saving energy compared to distillation.

(2) Possibilities of avoiding thermal degradation of the components.

(3) Prospects of more selective component separation.

(4) Development of improved devices for effective contacting of the liquid phases.

(5) Better understanding of the principles on the design and scale-up of extraction processes.

The liquid-liquid extraction system comprises three components: the solute or the material to be extracted; the solvent, which must not be completely miscible with the other liquids; and the "carrier" or nonsolute portion of the final mixture to be separated. In extraction, depending on the density of the solvent, the solvent can be the heavy phase or the light phase, the dispersed phase or continuous phase; but it will always be the extract phase. In simple definition, the solute passes from the raffinate ("carrier-rich") phase to the extract ("solvent-rich") phase. In counter-current liquid-liquid extraction, the heavy phase flows down and the light phase moves upward the column. The heavy phase most of the time is the dispersed phase and the light phase is the continuous phase. The physical properties (density, viscosity, and interfacial tension) of the two immiscible phases, raffinate and extract, have a greater influence on the capacity and efficiency of a liquid-liquid extraction process than the vapor-liquid properties in a distillation or stripping operation.

3. PROCESS FLOW

The pilot plant extraction unit is intended to remove the aromatic from the G.O. by using acetonitrile as the extracting solvents. The flowsheet of the process is shown in Figure 1.

The gas oil is pumped to the top of the column (V-1) through the rotameter R-1 from a burette (V-5), while the acetonitrile (Solvent) is pumped to the bottom of the column through rotameter R-2 from a burette (V-6). The extracting solvent which is the light phase and continuous phase moves upward through the packings (0.16 Propak S.S.) in the column while the gas oil which is the heavy phase and dispersed phase flow downward (counter-current) in the column. The solvent extract with the extracted aromatic comes out from the top of the column through the back-pressure BP-1 into the rectifying column (V-3) where the main bulk of the solvent (acetonitrile) is removed from the extract. From the top of V-3, the solvent flows through the condenser (H.E-1) and into the solvent reservoir (V-7). From the bottom of V-3A (thermosiphon reboiler), the extracted aromatics containing about 5% solvent flows to the stripping column V-4 where the remaining solvent is stripped by nitrogen, purged from bottom of the column. The stripped solvent goes to the condenser H.E-3 and down to the solvent reservoir V-7. The extract (solvent-free) from V-4A is collected and weighed for material balance. The raffinate (gas oil containing traced solvent and less aromatics) from V-1A goes through CV-1 (the liquid interphase control valve and CV-2 and to the top of the stripping column V-2 (falling-film evaporator). Nitrogen is introduced to the bottom of V-2 and it strips the solvents from the gas oil. The stripped solvent goes to the solvent reservoir via the condenser H.E-2.

The raffinate (solvent-free) from the bottom of V-2 is collected and weighed for material balance.

4. CONTROL

4.1 Temperature

The extraction column (V-1) is equipped with 1/4" copper coils around whereby cold water, hot water or steam can circulate around the column to control the desired temperature of extraction.

4.1 Pressure

The pressure of the extraction column is controlled by the back pressure, BP-1. It is a spring-o-ring type valve which opens at 60 psig.

4.3 Liquid Interface Level

The liquid interface level at the bottom of column V-1 is seen through Jerguson gauge V-1A and it is controlled by CV-1, DP-1 and CV-2 interaction.

4.4 Liquid Level in the Rectification Column

The liquid level in V-3 can be seen through V-3A and it is controlled by a dipleg and the metering valve 14.

Liquid level in the stripper column V-4 is also controlled by a dipleg in V-4A and the metering valve 16.

5. PRESSURE TESTING

Pressure test extraction column V-1 to 100 psig with nitrogen. Close valves 2, 8, 11, 12 and 21. Introduce nitrogen pressure through R-5 and open valves 5,6 and 7 at the bottom of the column.

Since V-2, V-3, V-3A, V-4, V-4A and V-7 will be operating virtually at atmospheric pressure, they should be pressure-tested at 25 psig with nitrogen after the contruction. Nitrogen pressure can be introduced through rotameters R-3 or R-4, and opening the connecting valve 14 and closing valves 11, 13, 15, 16, 9, 10 and 17, and plugging the vent of V-7.

6. START-UP

Open valves 3 and 4 and close valves 5 and 6. Start solvent pump P-2 and check the desired pumping rate through the burrette V-6. Continue pumping until the column V-1 is filled with solvent. This can be observed when the column is under pressure of about 75 psig. Close valve 11 and open valve 12. Solvent will start coming out through valve 12. Stop solvent pump P-2.

Open valve 1 and 2 and start pump P-1. Check the desired pumping rate and adjust the pumps vernier accordingly. When the heavy phase (raffinate oil) starts to appear at the bottom of V-1, in V-1A; start the solvent pump P-2 and open valves 5 and 7 and close valve 9 temporarily. Set LC-1 to the desired level as seen through V-1A. The level in V-8 will follow whatever level in V-1A. Open valves 20 and 32 and set the rotameter R-5 reading to about 2 on scale. PI-8 will assume a pressure reading of about 25 psig, because BP-2 has a cracking pressure of 25 psig. When a liquid level is about half-way in V-8, open valve 9 and the raffinate will flow into V-2 where the solvent is stripped overhead. Open the steam supply to V-2 and start nitrogen flow into the column through rotameter R-3. Raffinate (solvent-free) will come out of the bottom of V-2 through valve 10 and collected.

Open cooling water to H.E-2 and H.E-1 to C-1 and C-2. Open steam supply to V-3 and V-4. Open nitrogen supply to V-4 through rotameter R-4.

Close valve 12 and open valve 11. Now the extract (aromatic oil rich in solvent) will flow to V-3. Close valves 13 and 14. Watch for the liquid level in V-3A. When the liquid level in V-3A is above halfway, open valve 14. Now the extract containing less solvent will flow into V-4, the stripping column. The remaining solvent will be stripped overhead and flows into H.E-1 together with the main bulk of the solvent from V-3. The recovered solvent flows into the solvent reservoir V-7, and is recycled back to the extraction column V-1. The extract (solvent-free) flows to the bottom of the column V-4 and accumulates in V-4A. The level of the extracted oil in V-4A is maintained through a dip-leg and regulated by valve 16. The extract is collected from valve 16 and weighed.

Now the extraction unit is on steam. Regular reading of the temperature profile (T1-1,2,3) of the columnn is taken regularly and the feed rates of the solvent and G.O. are recorded from the burrettes. The raffinate and extract are collected at regular interval and weighed. The desired temperature profile of the column can be adjusted by running cold water, hot water or steam through the coils wrapped around the column (V-1). During the operation, suction hood will always be running at the bottom of V-2 and V-4.

7. NORMAL SHUT-DOWN

Close valves 1 and 3 and shut down feed pumps P-1 and P-2. Close valves 11 and 9 and open valves 12 and 8, and V-1 column will drain. Drainage from the unit containing the solvent (accetonitrile) is dumped into a special drum for special disposal unit. Steam supply to VC-2, V-3 and V-4 is cut-off when the oil is completely drained from each column and the nitrogen supply can also be closed.

8. EMERGENCY SHUT-DOWN

8.1 If column (V-1) pressure builds up above the operating pressure, it could be due to restriction down stream in column V-2, V-3 or V-4. Most likely it could be the plugging of BP-1. Shut down the feed pumps P-1 and P-2. Depressurize the column by opening by-pass valve 6 and valve 8. Remove BP-1 valve and check for restriction. Relief valve RV-3 will open when pressure reaches 100 psig.

8.2 If column (V-1) pressure is coming down, stop feed pumps (P-1 and P-2) and check for leaks. Also check if pumps are operating.

8.3 In case of fire, switch off the main power supply and get hold of fire extinguisher immediately. If fire is beyond control, switch on the fire alarm and run out of the building.

9. EQUIPMENT LISTS

List of Vessels

Number	Description
V-1	Extraction column. 1" diameter and 16' tall, s.s tubing filled with "Propak" packings, 0.16" size.
V-1A	Jerguson Gauge at bottom of V-1
V-2	Falling-film evaporation, for stripping the solvent from the raffinate.
V-3	Rectifying column, 1" diameter and 6' tall, filled with S.S. "Propak" packings, 0.16" size.
V-3A	Jerguson gauge at the bottom of V-3 and the thermosiphon reboiler of V-3.
V-4	Stripping column, 1" diameter and 6' tall, filled with S.S. "Propak" packings, 0.16" size.
V-4A	Jerguson gauge at the bottom of V-4
V-5	Burrette feed for pump P-1 (G.O.)
V-6	Burrette feed for pump P-2 (Solvent)
V-7	Solvent reservoir (10 gals capacity).
V-8	Jerguson gauge bubbler for DP-1.

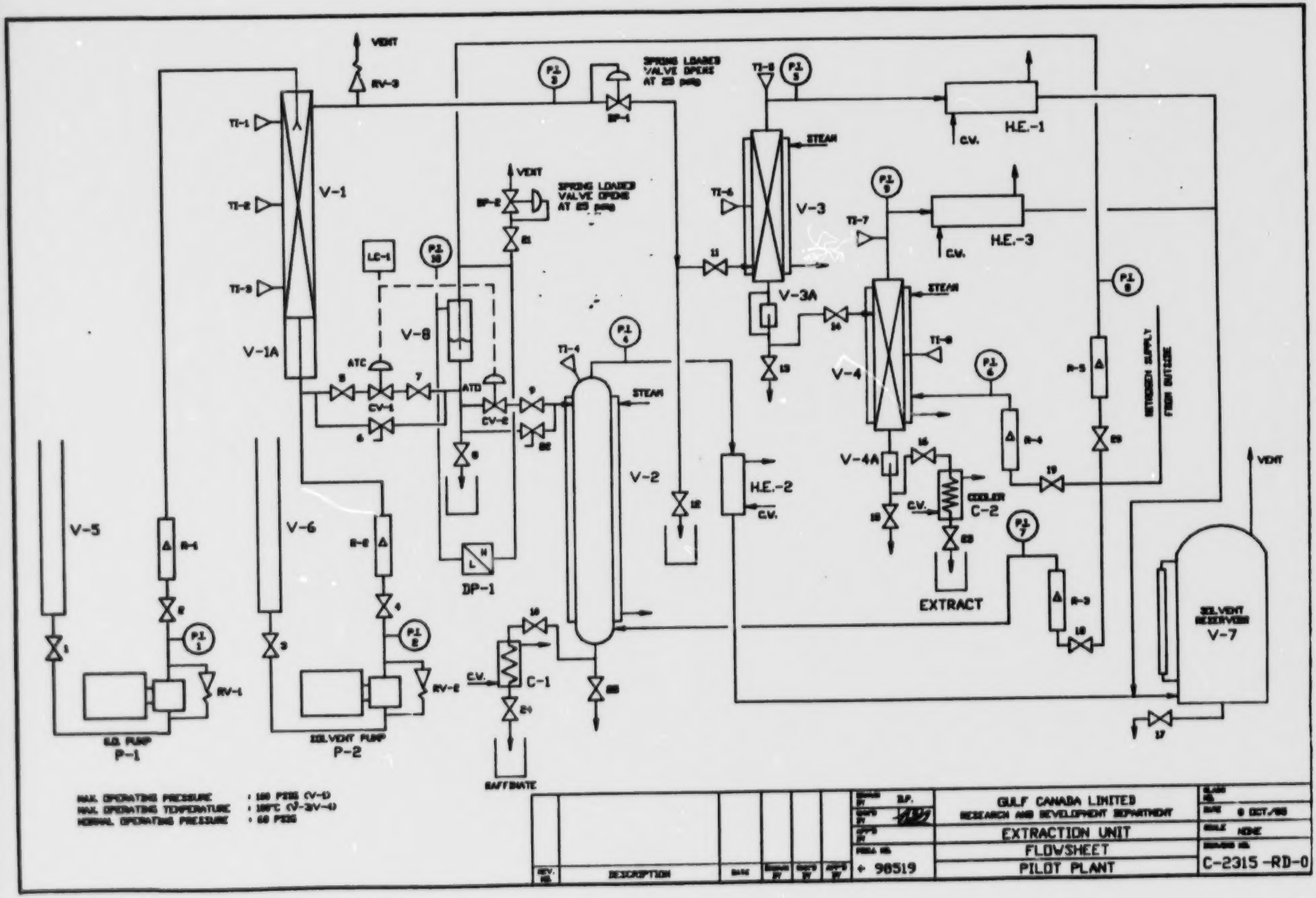
List of Heat Exchangers

H-E-1	Condenser for the solvent from rectifying column V-3
H-E-2	Condenser for the solvent from falling-film evaporator (V-2)
H-E-3	Condenser for the solvent from stripping column V-4
C-1	Raffinate Cooler
C-2	Extract Cooler

Number	Description
List of Pumps	
P-1	Metering feed pump for G.O.
P-2	Metering feed pump for solvent
List of Pressure Gauges	
PI-1	Discharge pressure for pump P-1
PI-2	Discharge pressure for pump P-2
PI-3	Pressure gauge for extraction column V-1
PI-4	Pressure gauge for V-2
PI-5	Pressure gauge for V-3
PI-6	Pressure gauge for N_2 supply to V-4
PI-7	Pressure gauge for N_2 supply to V-2
PI-8	Pressure gauge for N_2 supply to bubbler V-8
List of Controllers	
LC-1	Liquid-interface controllers for V-11 and V-8
CV-1	Control valve for V-1A, ATC
CV-2	Control valve for V-8, ATO
DP-1	D/P cell to sense the liquid interface in V-8 and indirectly V-1A.

Number	Description
List of Rotameters	
R-1	Flow indicator of feed pump P-1 (G.O.)
R-2	Flow indicator of feed pump P-2 (solvent)
R-3	N_2 flow indicator to V-2
R-4	N_2 flow indicator to V-4
R-5	N_2 flow indicator to V-8
List of Temperature Indicator	
T1-1) T1-2) T1-3)	Temperature profile of the extraction column V-1 from top to bottom.
T1-4	Top temperature of V-2
T1-5	Top temperature of V-3
T1-6	Wall temperature of V-3
T1-7	Top temperature V-4
T1-8	Wall temperature of V-4
List of Valves	
RV-1	Relief valve for pump P-1
RV-2	Relief valve for pump P-2
RV-3	Relief valve for the column V-1
BP-1	Back-pressure control valve of V-1
BP-2	Back pressure valve of V-8
1	Outlet valve for feed burrette V-5
2	Discharge valve for pump P-1
3	Outlet valve for feed burrette V-6
4	Discharged valve for pump P-2

Number	Description
5	Block valves for CV-1
6	By-pass valve for CV-1
7	Block valve for CV-1
8	Drain valve for V-8
9	Block valve for Cv-2
10	Drain valve for V-2 to cooler C-1
11	Connecting valve or feed valve to V-3 from V-1
12	Drain valve for overhead product from V-1
13	Drain valve for V-3A
14	Feed valve to V-4 from V-3
15	Drain valve of V-4A
16	Product drain valve of V-4
17	Drain valve for solvent reservoir, V-7
18	N_2 supply valve to V-2
19	N_2 supply valve to V-4
20	N_2 supply valve to V-8
21	Block valve to BP-2
22	By-pass needle valve for CV-2
23	Drain valve for C-2 cooler
24	Drain valve for C-1 cooler
25	Drain valve for V-2 bottom


VENT
RV-3
SPRING LOADED VALVE OPENS AT 25 psig
BP-1
V-1
V-1A
TI-1
TI-2
TI-3
LC-1
V-8
BP-2
SPRING LOADED VALVE OPENS AT 25 psig
ATC
ATD
CV-1
CV-2
TI-4
STEAM
V-2
DP-1
V-3
V-3A
TI-6
TI-7
H.E.-1
H.E.-3
C.V.
V-4
V-4A
TI-8
H.E.-2
COOLER C-2
EXTRACT
NITROGEN SUPPLY FROM OUTSIDE
V-5
V-6
C-1
RAFFINATE
SOLVENT RESERVOIR V-7
SOLVENT PUMP P-1
SOLVENT PUMP P-2
MAX. OPERATING PRESSURE : 100 PSIG (V-1)
MAX. OPERATING TEMPERATURE : 150°C (V-2/V-4)
NORMAL OPERATING PRESSURE : 60 PSIG
GULF CANADA LIMITED
RESEARCH AND DEVELOPMENT DEPARTMENT
EXTRACTION UNIT
FLOWSHEET
PILOT PLANT
+ 98519
C-2315-RD-0
DESCRIPTION

APPENDIX II

Evaluation of Middle Distillate - Organic Solvent Phase Diagram Data - Illustrative Calculation

The material balance and tie-lines calculations mentioned in Section 4.3.1 for middle distillate-organic solvent systems were conducted as illustrated below:

Experiment #103: Extraction of Syncrude Middle Distillate with Acetonitrile at 20°C, nominal solvent/oil ratio = 1.7 vol/vol.

Feed weight:	169.0 g
Aromatics content of the feed:	40.44 wt.%
Solvent weight:	266.0 g
Weight of recovered raffinate phase:	141.7 g
Density of recovered raffinate phase:	0.8520 g/mL
Aromatics content of the raffinate hydrocarbons:	31.61 wt.%
Solvent content of the raffinate phase:	2.35 vol.%
Solvent density:	0.787 g/mL

Calculations:

Wt.% solvent in the raffinate phase:	$\frac{0.787 \times 2.35}{0.8520} = 2.17$
Hydrocarbons in the raffinate phase:	141.7 x (1-0.0217) = 138.6 g
Hydrocarbons in the extract phase:	169.0 - 138.6 = 30.4 g
Aromatics in the raffinate phase:	138.6 x 0.3161 = 43.8 g
Aromatics in the extract phase:	0.4044 x 169.0 - 43.8 = 24.5 g
Solvent in the extract phase:	266.0 - 141.7 x 2.17/100 = 262.9 g
Wt.% aromatics in the raffinate phase:	100 x 43.8/141.7 = 30.91
Wt.% non-aromatics in the raffinate phase:	100 - 30.91 - 2.17 = 66.92
Wt.% aromatics in the extract phase:	24.5/(30.4 + 262.9) = 8.35
Wt.% solvent in the extract phase:	262.9/(30.4 + 262.9) = 89.64
Wt.% non-aromatics in the extract phase:	100 - 8.35 - 89.64 = 2.01

APPENDIX III

Hand-Bancroft Consistency Tests for Phase Equilibrium Data

Figures III.1 to III.3* are Hand-Bancroft consistency tests (41,42) for the SO_2 extraction of Syncrude middle distillate at -12°C, +2°C and +17°C (Table 4.2). Similarly, Figures III.4 to III.6 provide checks on the Suncor middle distillate extractions at three temperatures (Table 4.3). Figures III.7-III.13 are analogous plots for the acetonitrile data of Tables 4.4 and 4.5 (SYN = Syncrude, SUN = Suncor), and Figures III.14-III.19 correspond to Tables 4.6 and 4.7 (dimethylformamide extractions). Acceptably straight lines have been obtained - or at least one could not justify discarding any particular experimental point. (Those results that were shown to be suspect via the initial Hand-Bancroft tests, have been excluded from Tables 4.2 to 4.7 and from the final plots given here.)

*These first three figures "spell out" the quantities plotted on the ordinates and abscissas; in the remaining graphs of the present appendix they are the same but are identified in accordance with Treybal's notation (29).

FIGURE III.1

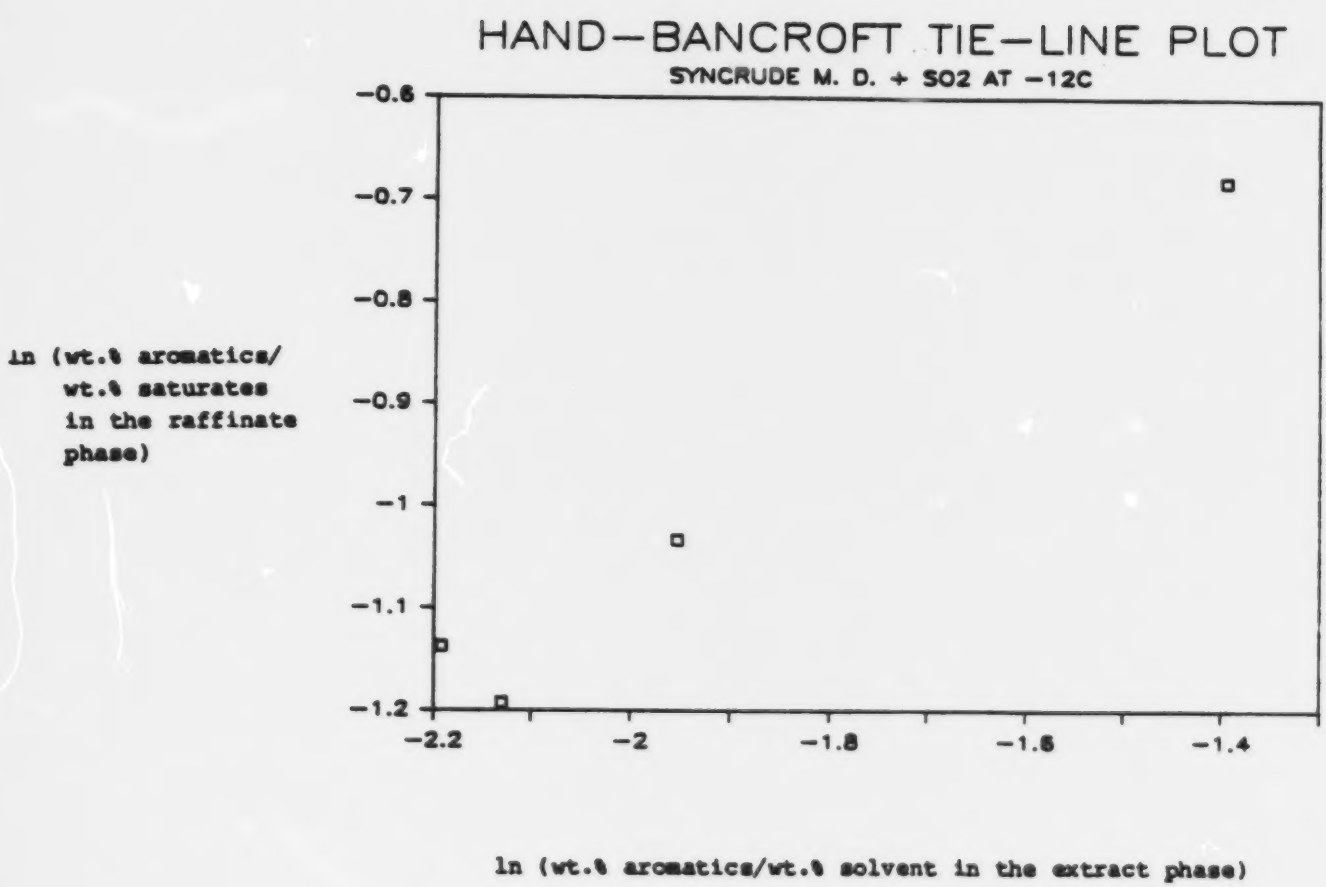

HAND—BANCROFT TIE—LINE PLOT
SYNCRUDE M. D. + SO2 AT −12C
−0.6
−0.7
−0.8
−0.9
−1
−1.1
−1.2
−2.2
−2
−1.8
−1.6
−1.4
ln (wt.% aromatics/ wt.% saturates in the raffinate phase)
ln (wt.% aromatics/wt.% solvent in the extract phase)

FIGURE III.2

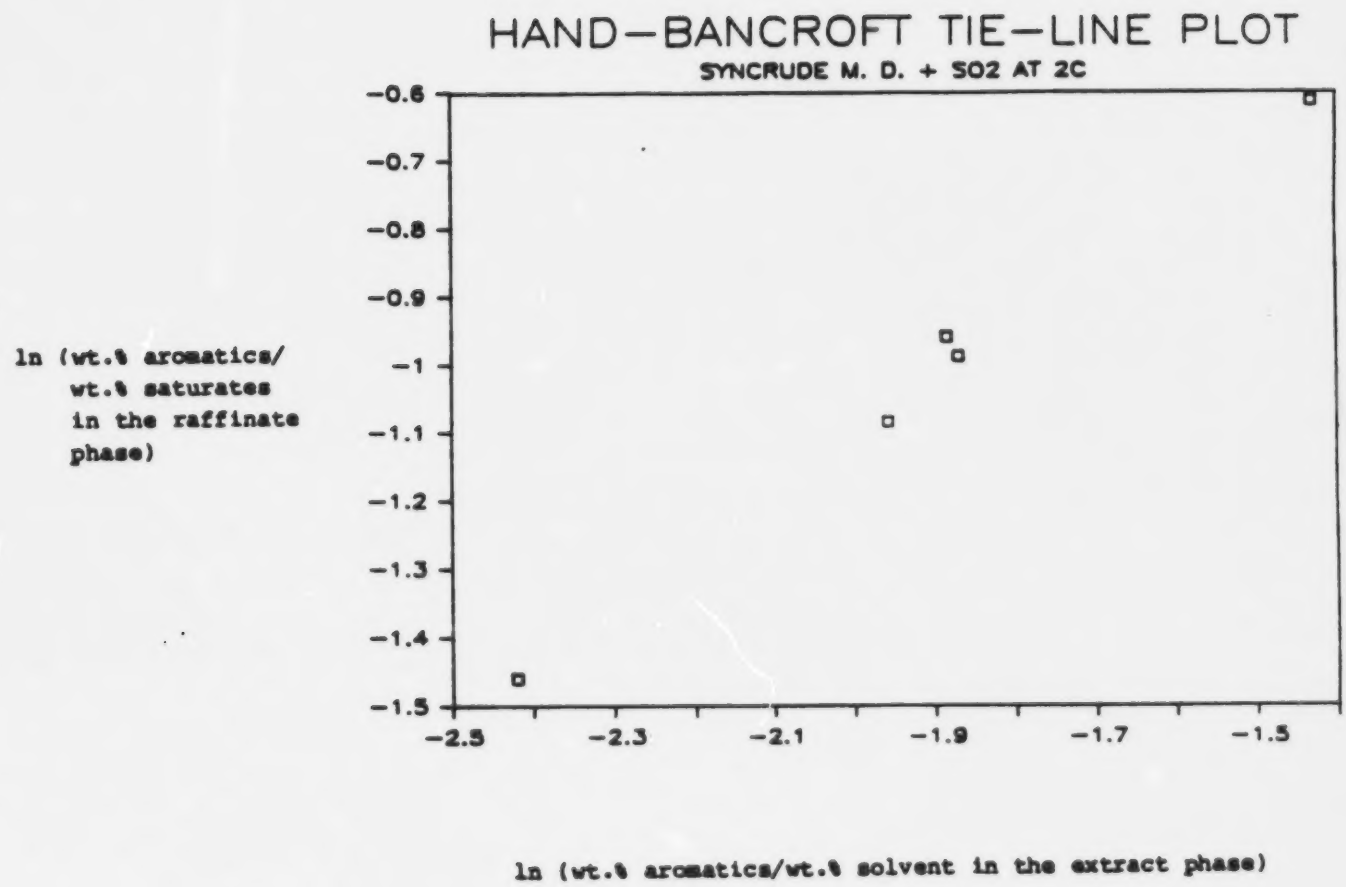

HAND—BANCROFT TIE—LINE PLOT
SYNCRUDE M. D. + SO2 AT 2C
ln (wt.% aromatics/ wt.% saturates in the raffinate phase)
-0.6
-0.7
-0.8
-0.9
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-2.5
-2.3
-2.1
-1.9
-1.7
-1.5
ln (wt.% aromatics/wt.% solvent in the extract phase)

FIGURE III.3

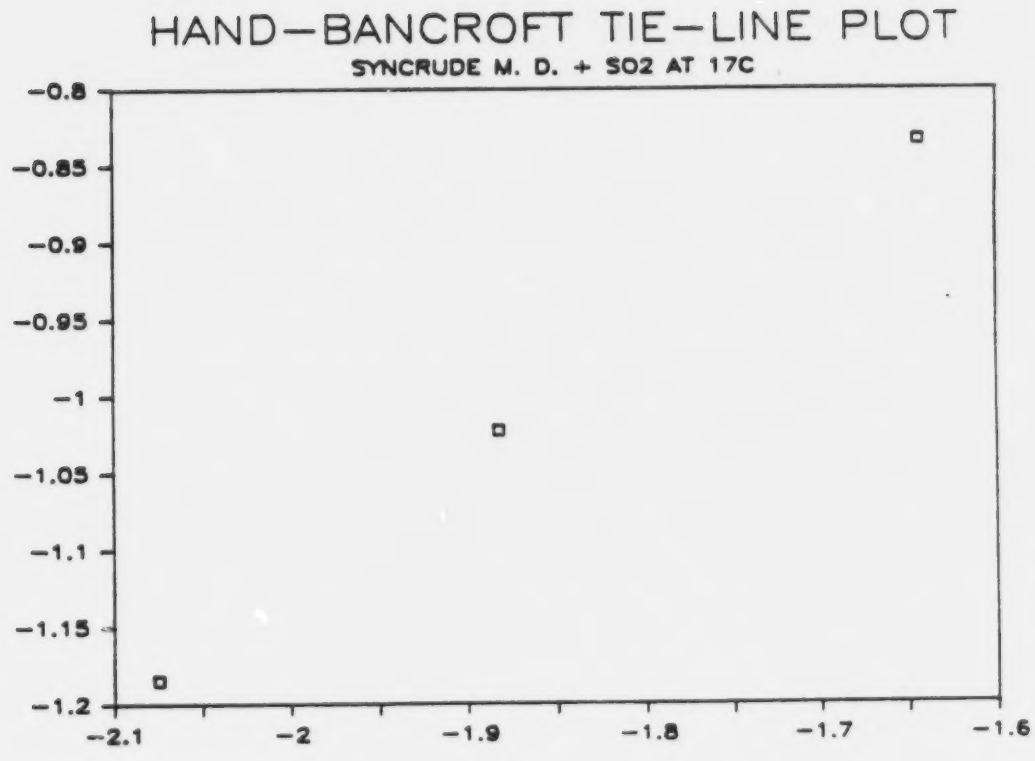

HAND—BANCROFT TIE—LINE PLOT
SYNCRUDE M. D. + SO2 AT 17C
-0.8
-0.85
-0.9
-0.95
-1
-1.05
-1.1
-1.15
-1.2
-2.1
-2
-1.9
-1.8
-1.7
-1.6
ln (wt.% aromatics/
/t.% saturates
in the raffinate
phase)
ln (wt.% aromatics/wt.% solvent in the extract phase)

FIGURE III.4

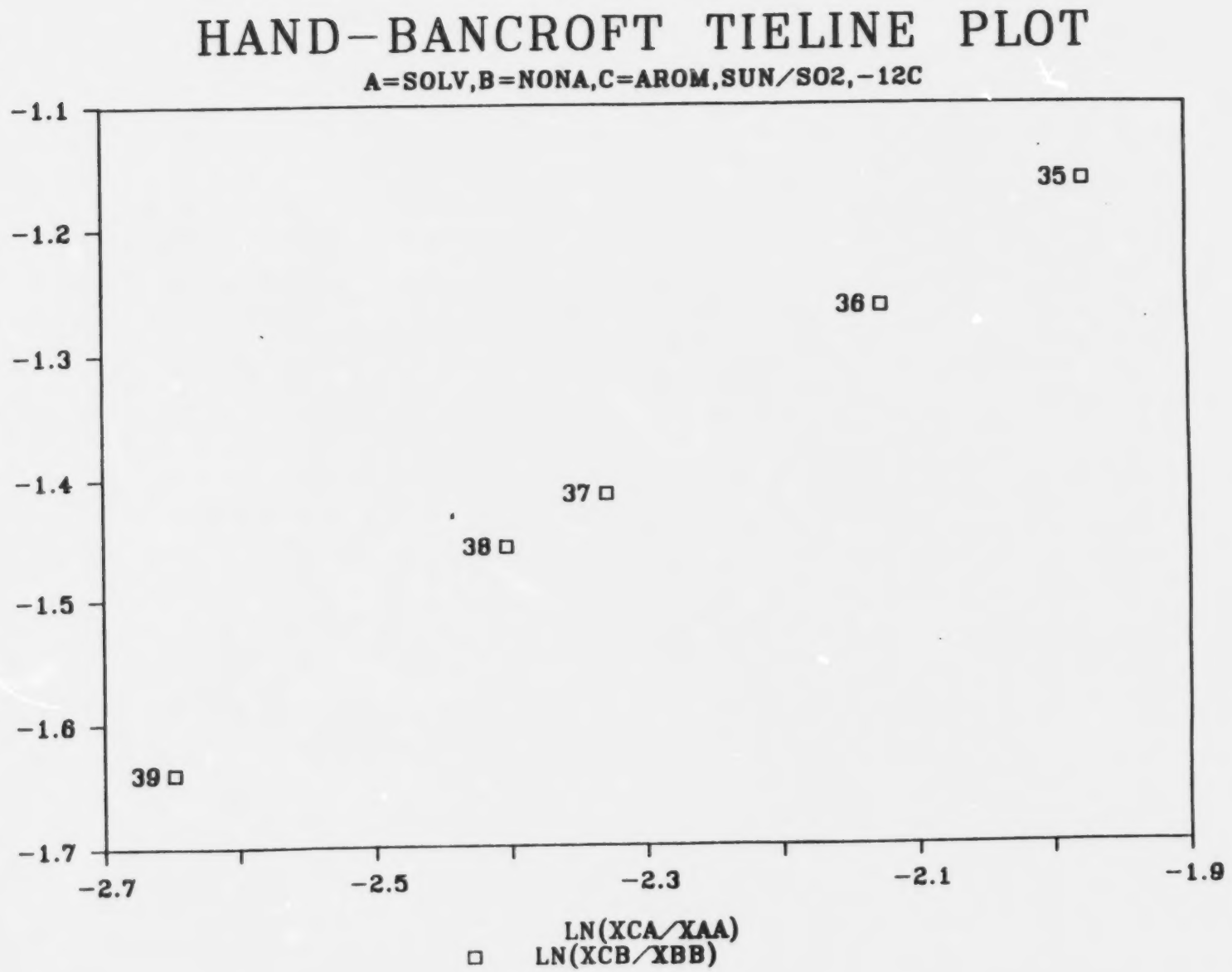

HAND-BANCROFT TIELINE PLOT
A=SOLV,B=NONA,C=AROM,SUN/SO2,-12C
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
-1.7
35
36
37
38
39
-2.7
-2.5
-2.3
-2.1
-1.9
LN(XCA/XAA)
LN(XCB/XBB)

FIGURE III.5

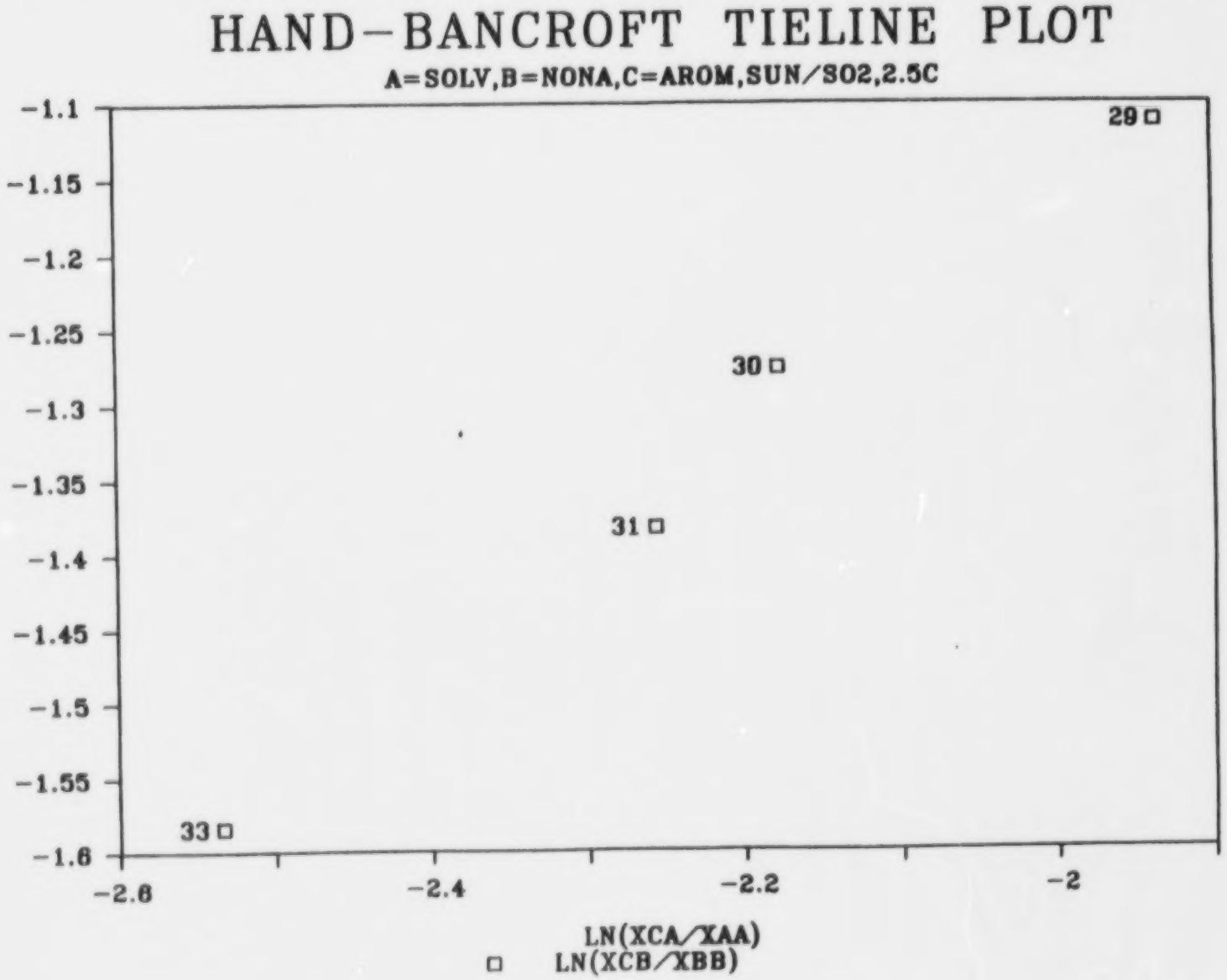

HAND-BANCROFT TIELINE PLOT
A=SOLV,B=NONA,C=AROM,SUN/SO2,2.5C
-1.1
-1.15
-1.2
-1.25
-1.3
-1.35
-1.4
-1.45
-1.5
-1.55
-1.6
29
30
31
33
-2.6
-2.4
-2.2
-2
LN(XCA/XAA)
LN(XCB/XBB)

FIGURE III.6

HAND–BANCROFT TIELINE PLOT

A=SOLV,B=NONA,C=AROM,SUN/SO2,17.5C

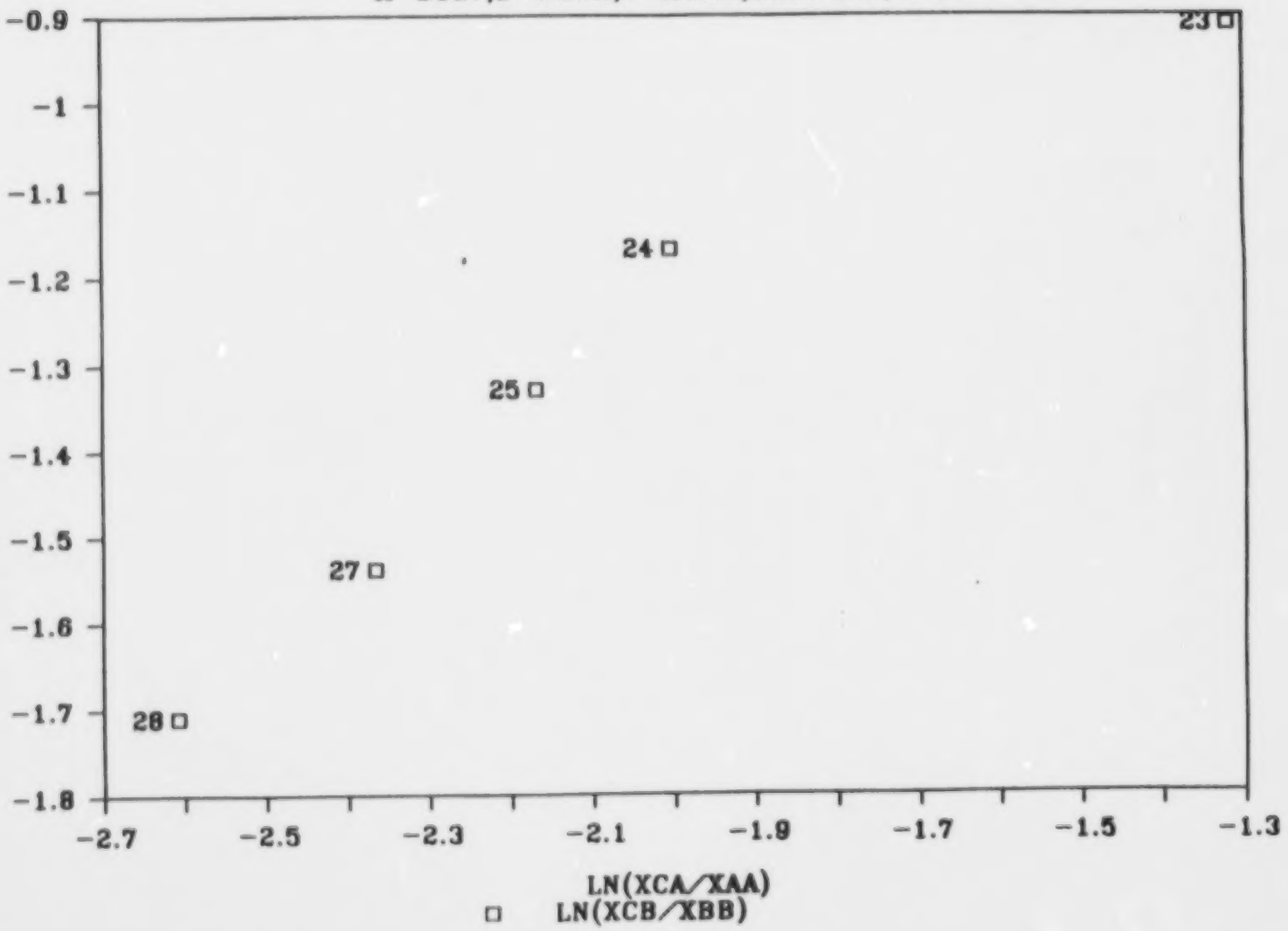


FIGURE III.7

HAND–BANCROFT TIELINE PLOT

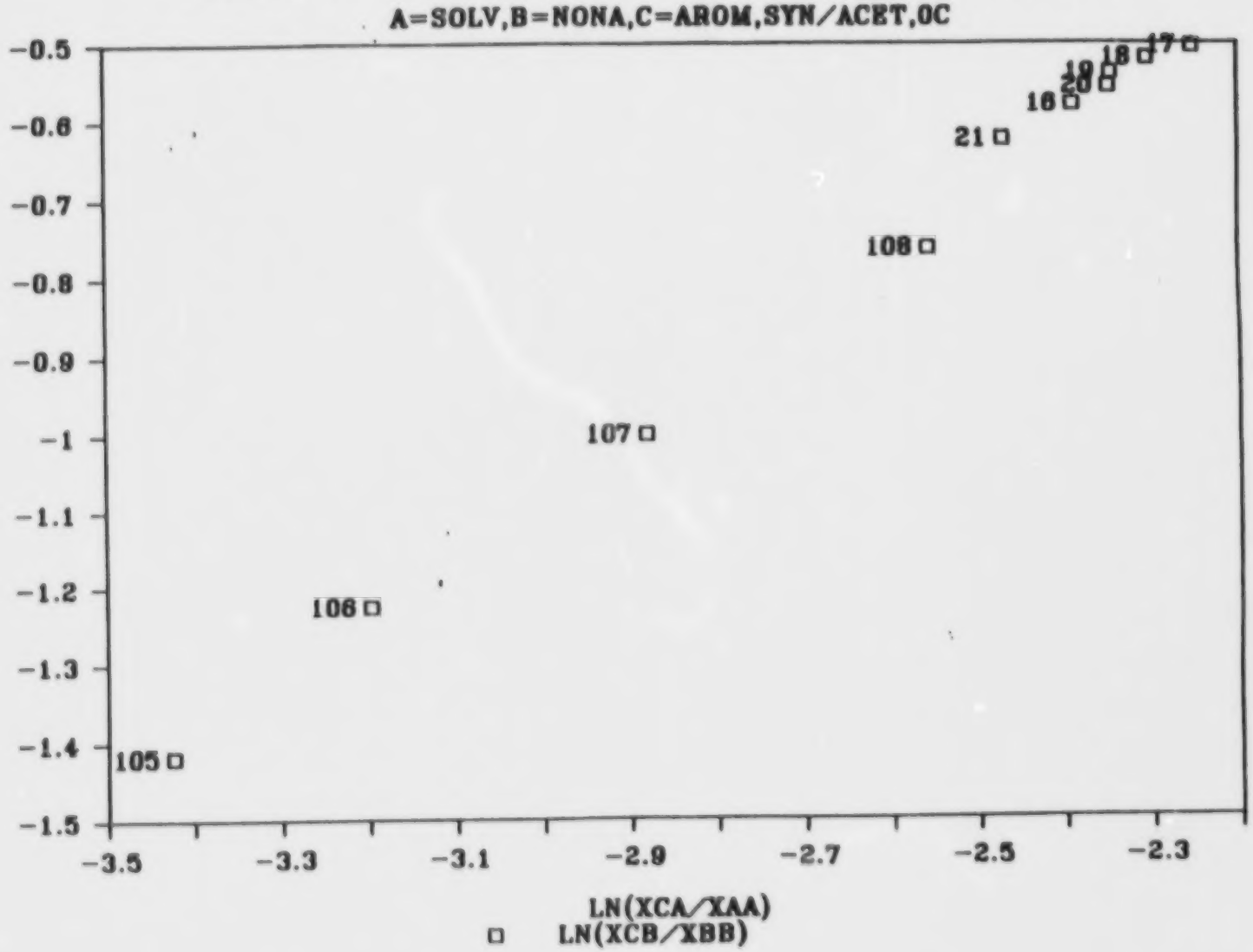


FIGURE III.8

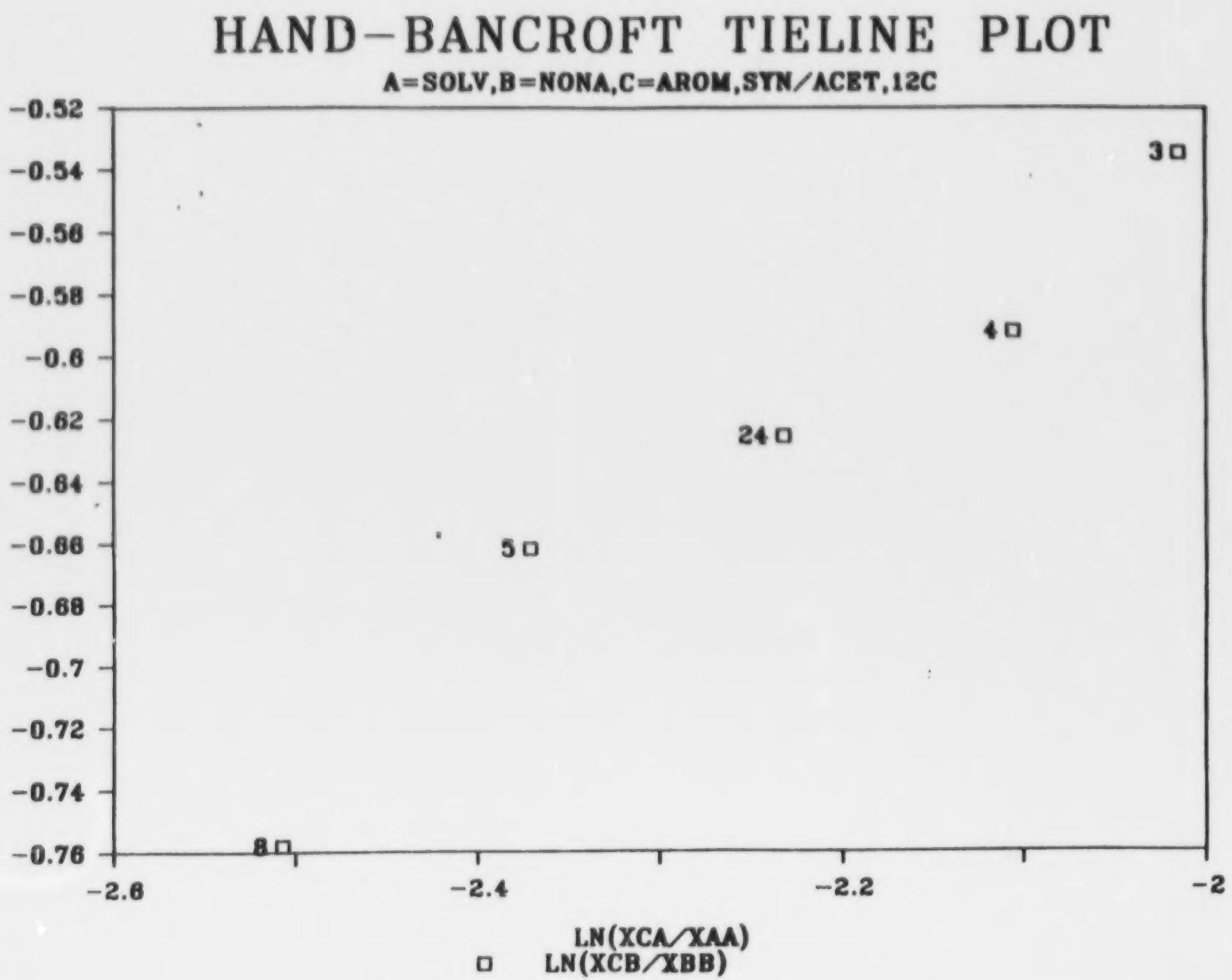

HAND-BANCROFT TIELINE PLOT
A=SOLV,B=NONA,C=AROM,SYN/ACET,12C
-0.52
-0.54
-0.56
-0.58
-0.6
-0.62
-0.64
-0.66
-0.68
-0.7
-0.72
-0.74
-0.76
-2.6
-2.4
-2.2
-2
3
4
24
5
8
LN(XCA/XAA)
LN(XCB/XBB)

FIGURE III.9

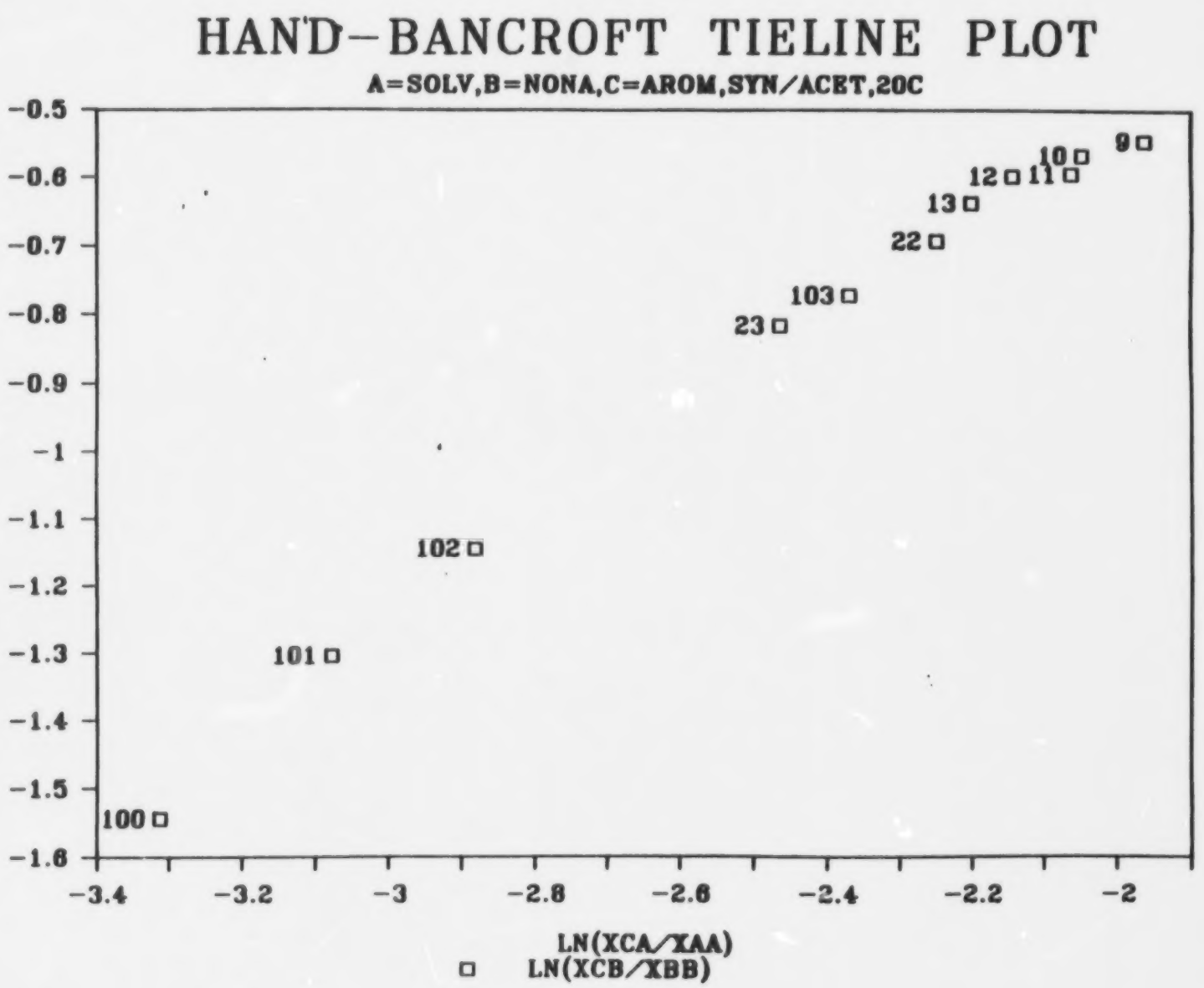

HAND–BANCROFT TIELINE PLOT
A=SOLV,B=NONA,C=AROM,SYN/ACET,20C
-0.5
-0.6
-0.7
-0.8
-0.9
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
-3.4
-3.2
-3
-2.8
-2.6
-2.4
-2.2
-2
9
10
12
11
13
22
103
23
102
101
100
LN(XCA/XAA)
LN(XCB/XBB)

FIGURE III.10

HAND–BANCROFT TIELINE PLOT

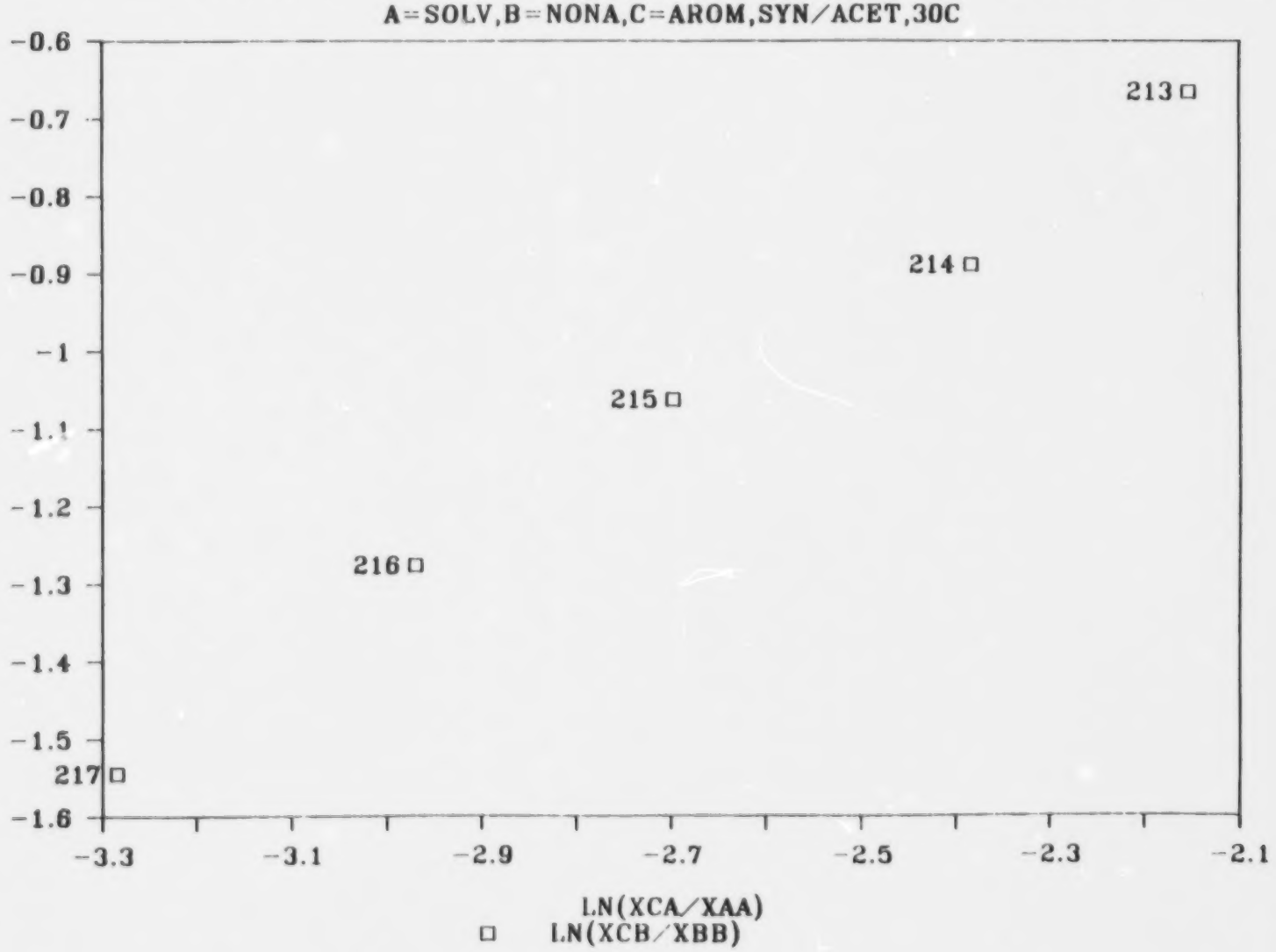


FIGURE III.11

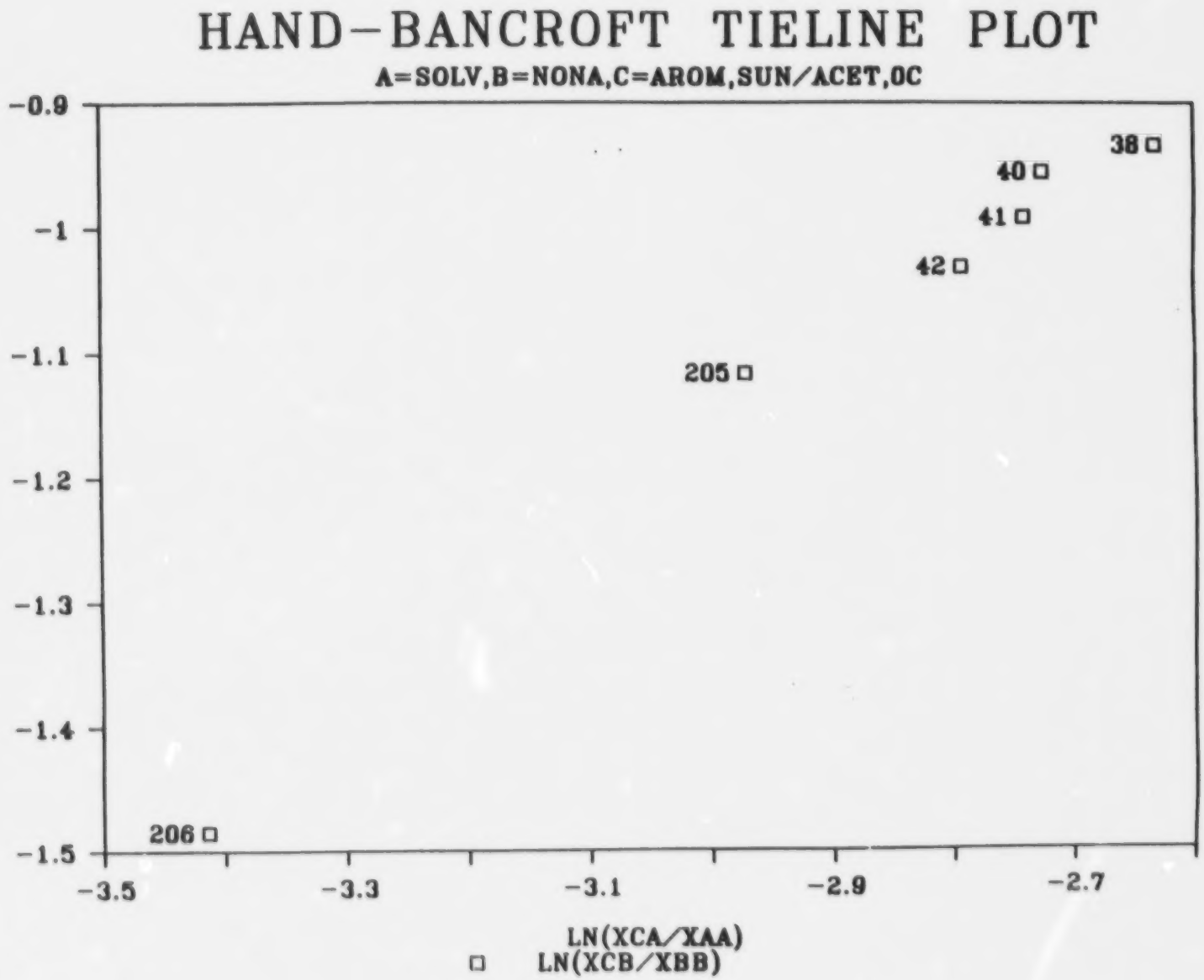


FIGURE III.12

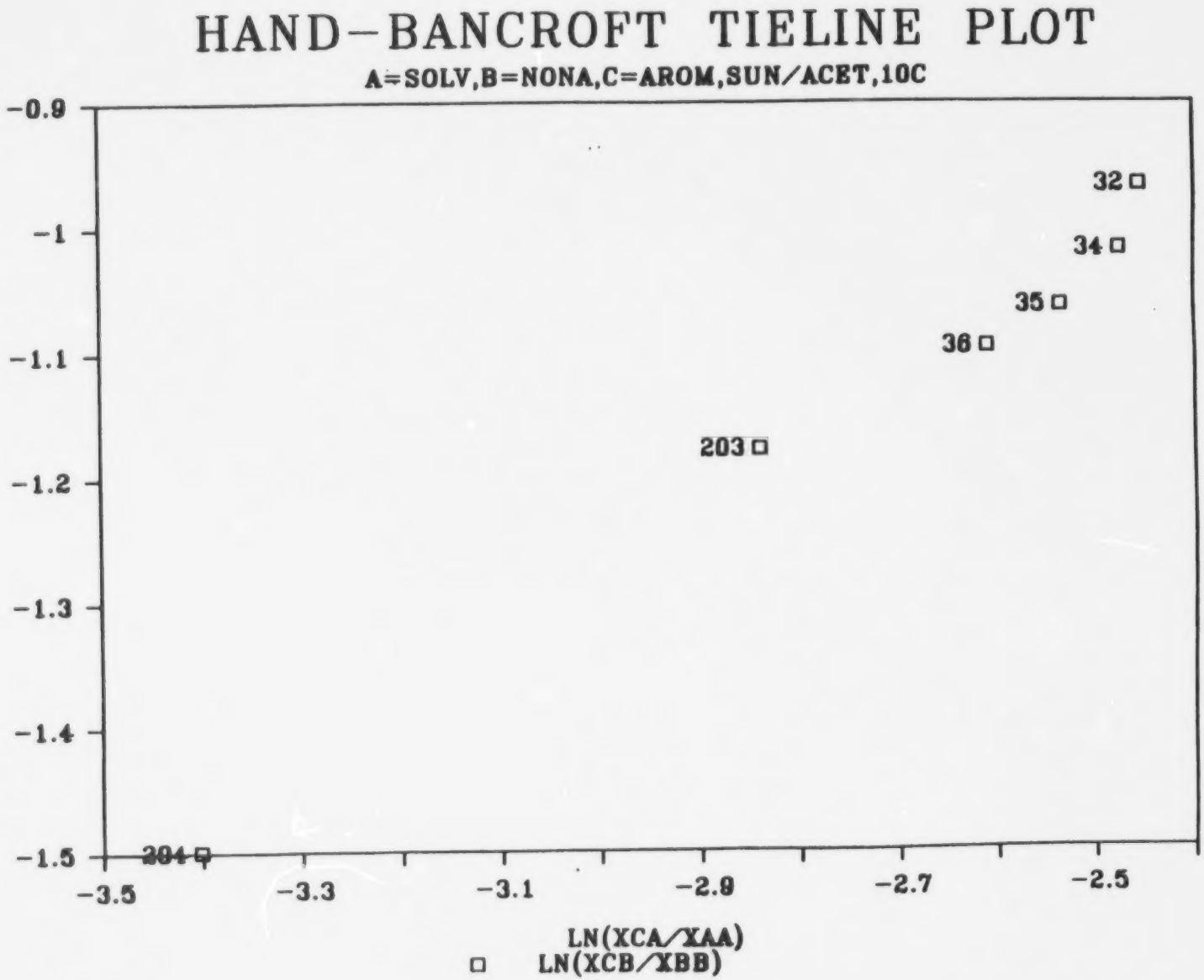


FIGURE III.13

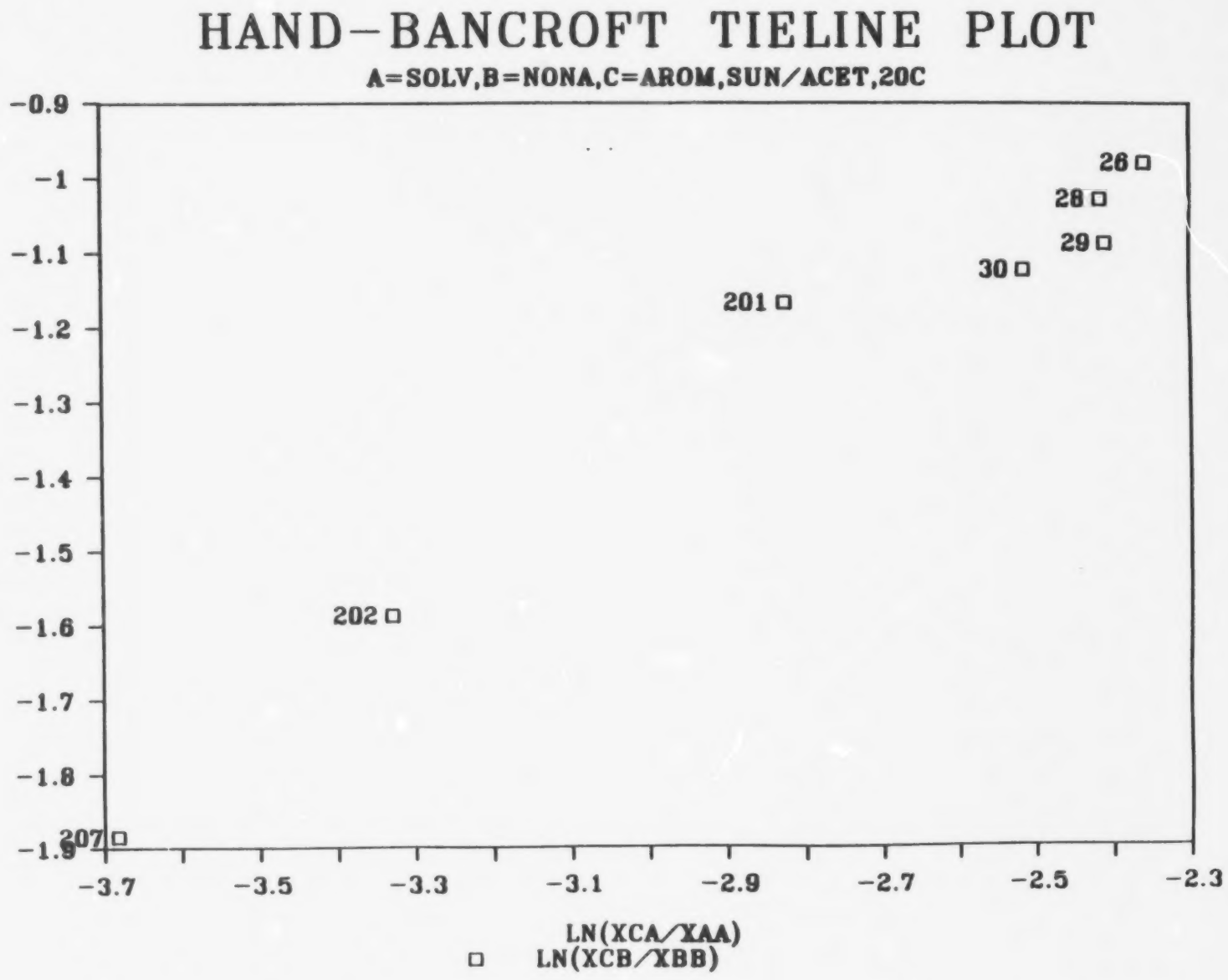


FIGURE III.14

HAND–BANCROFT TIELINE PLOT

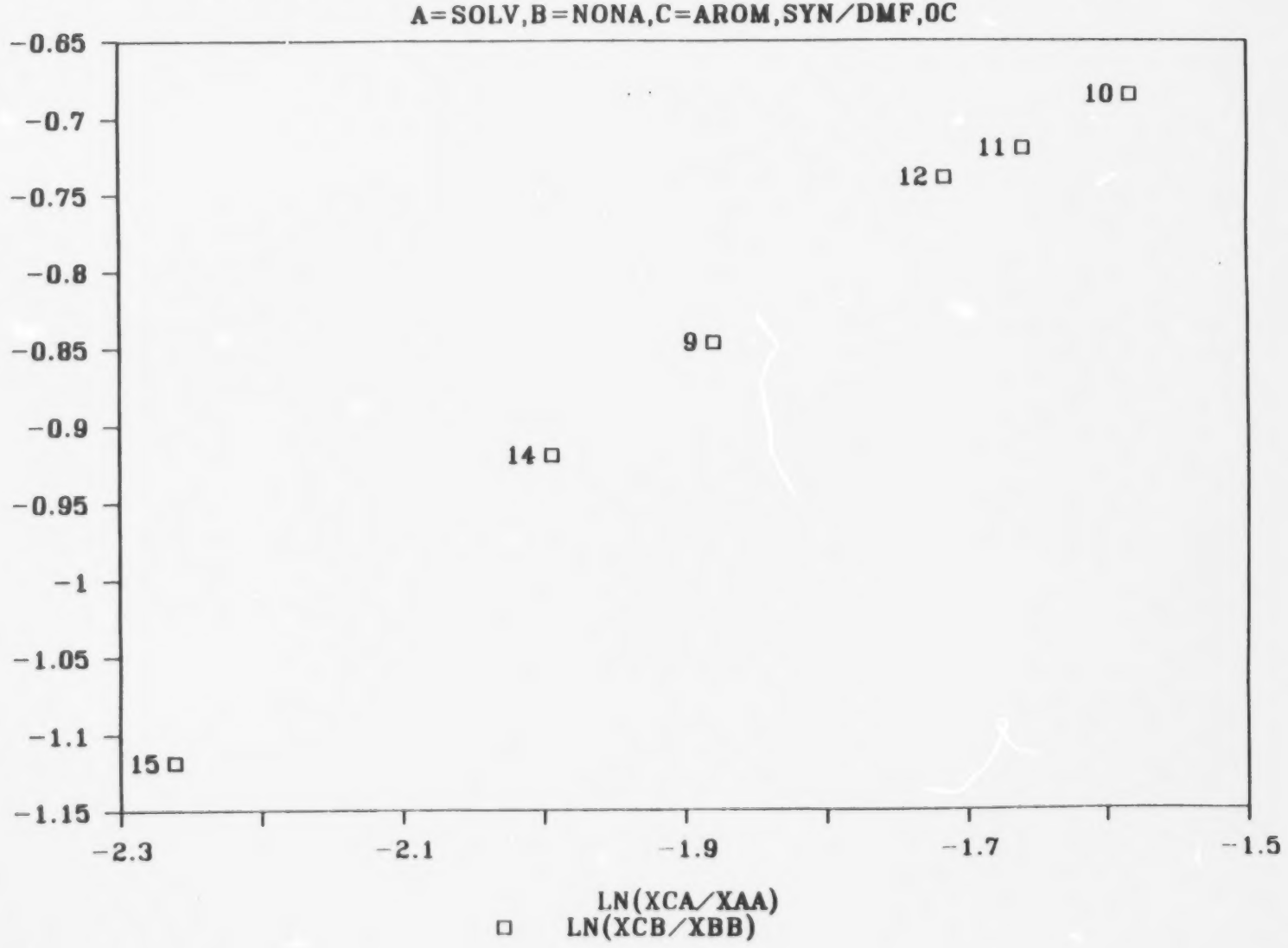


FIGURE III.15

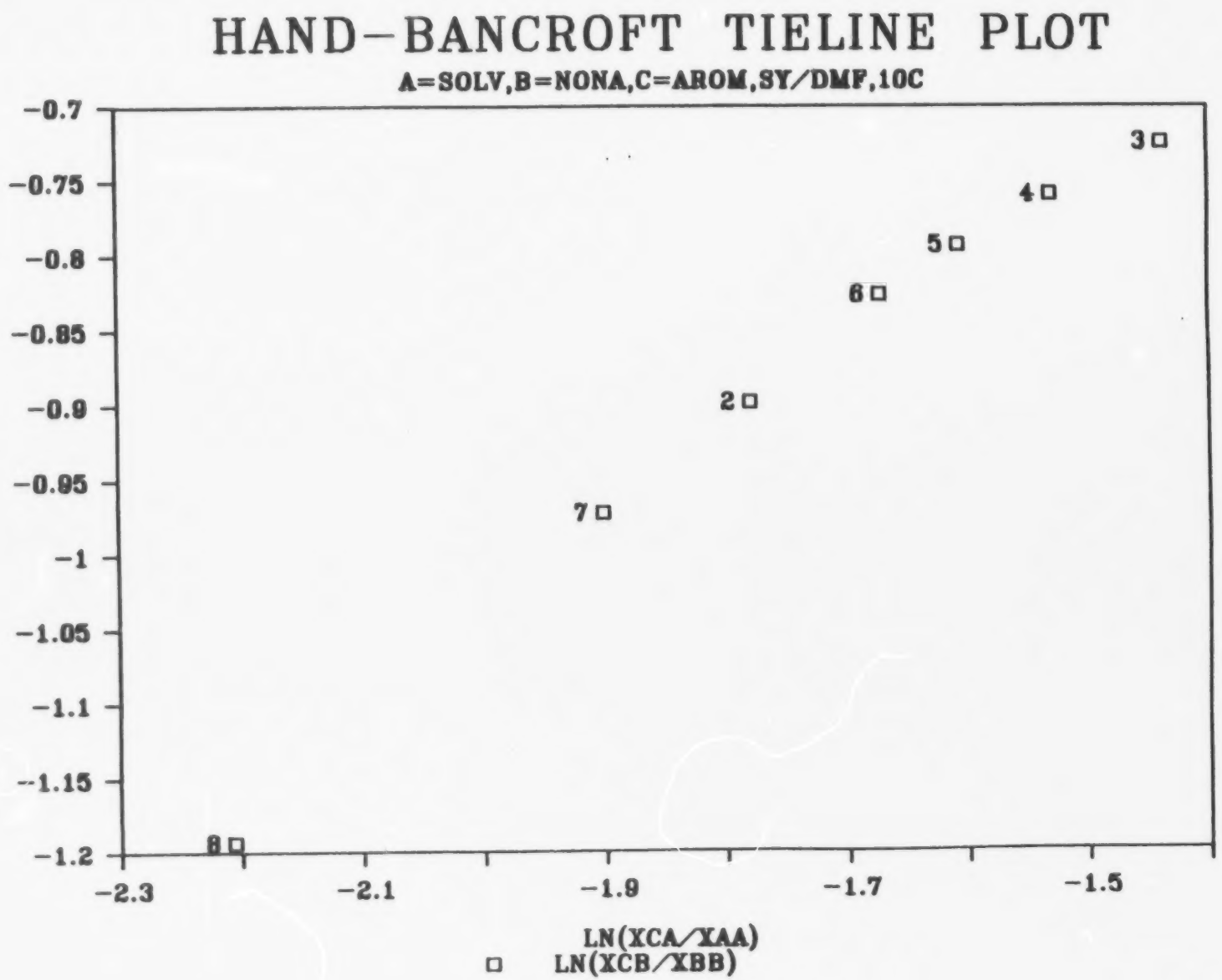


FIGURE III.16

HAND–BANCROFT TIELINE PLOT

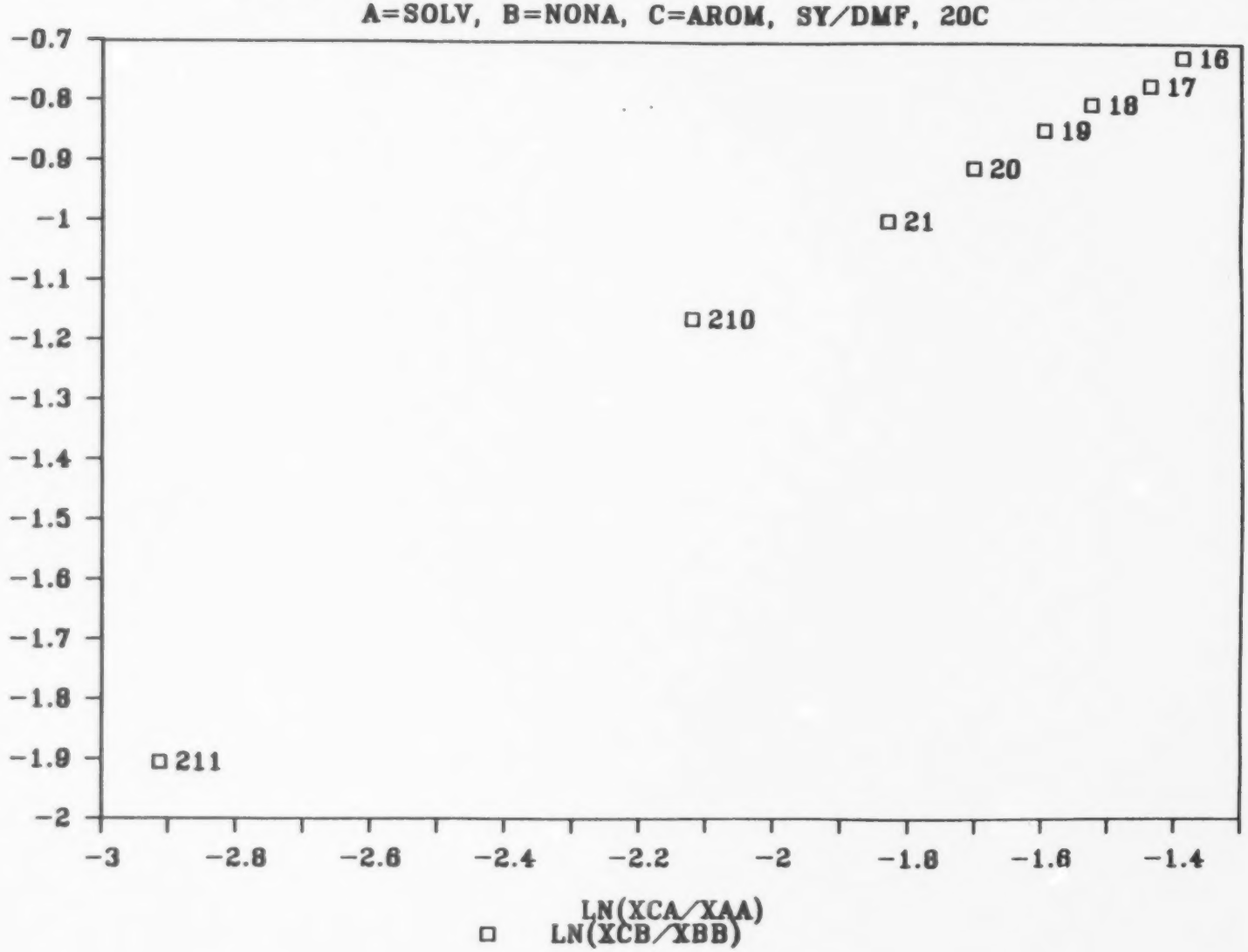


FIGURE III.17

HAND–BANCROFT TIELINE PLOT

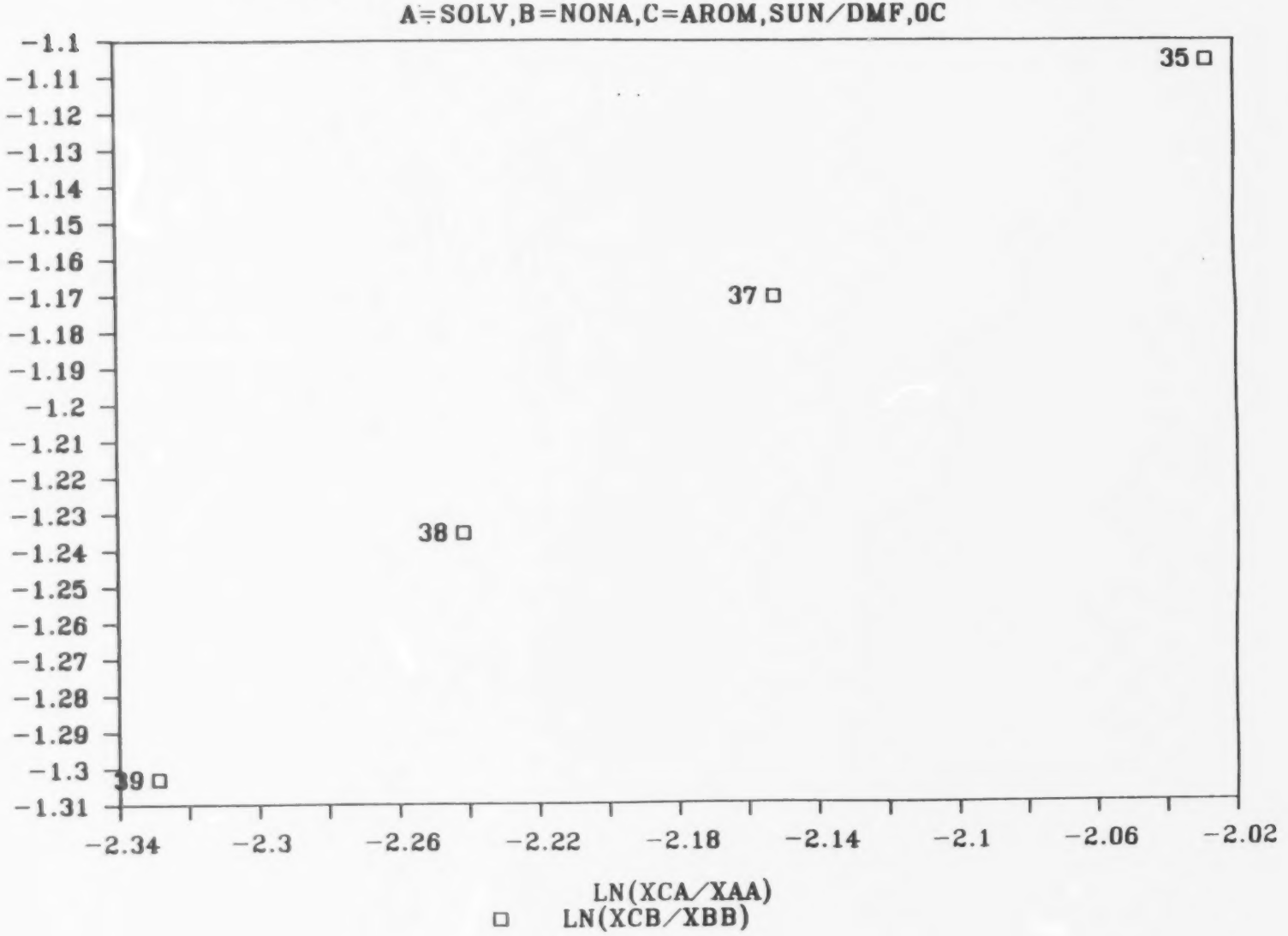


FIGURE III.18

HAND BANCROFT TIELINE PLOT

SUNCOR/DMF,10C

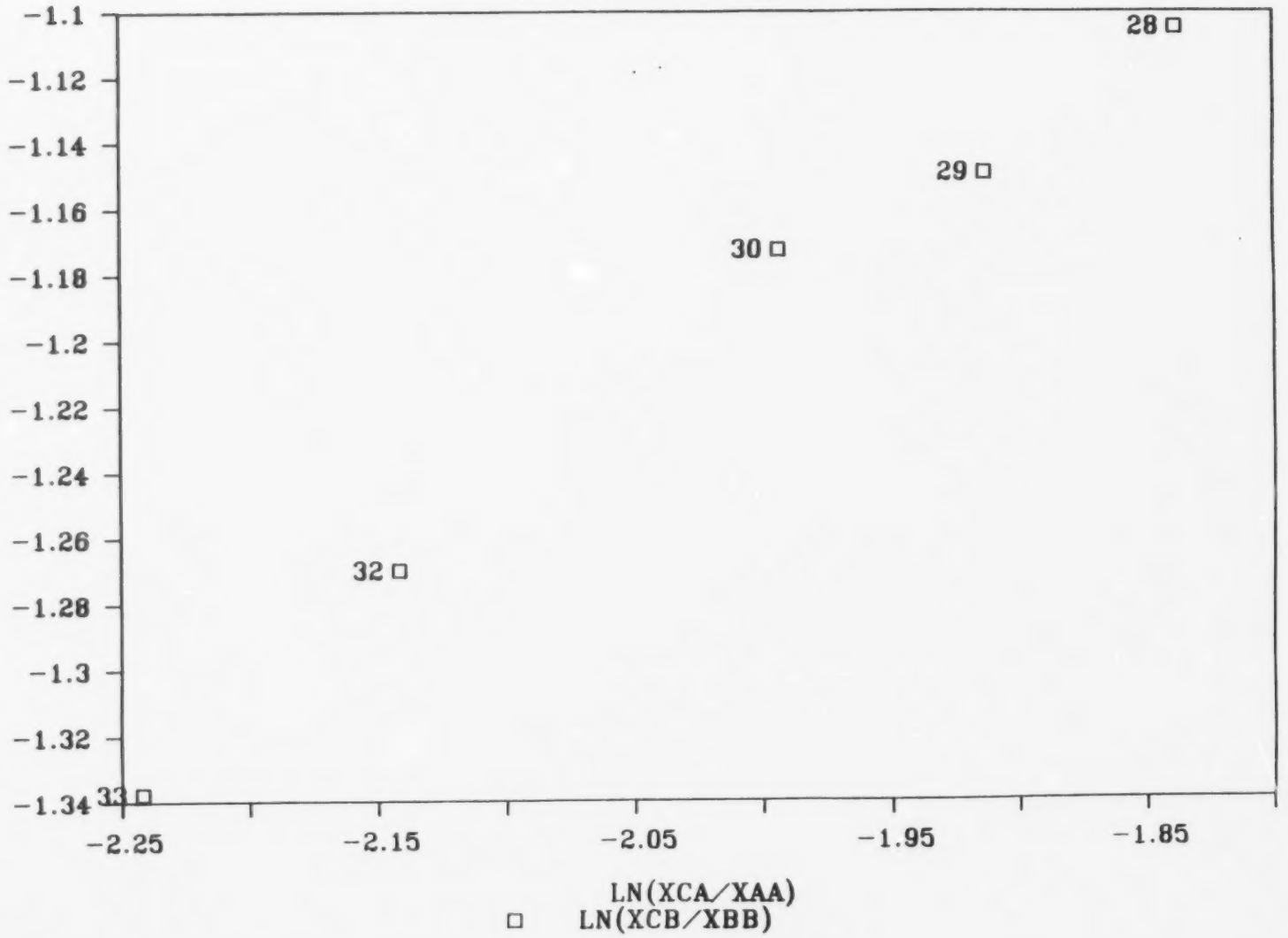
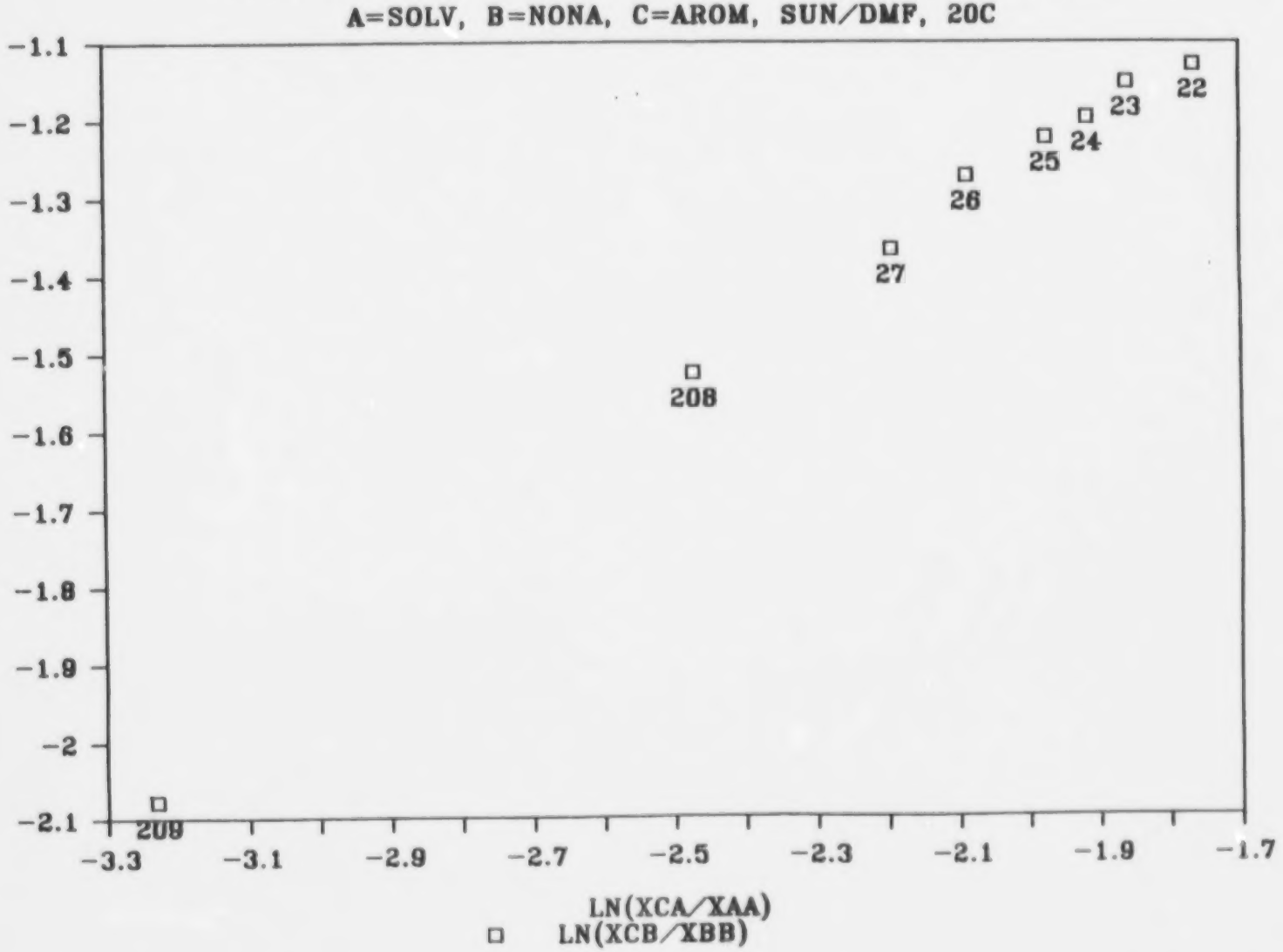


FIGURE III.19

HAND–BANCROFT TIELINE PLOT

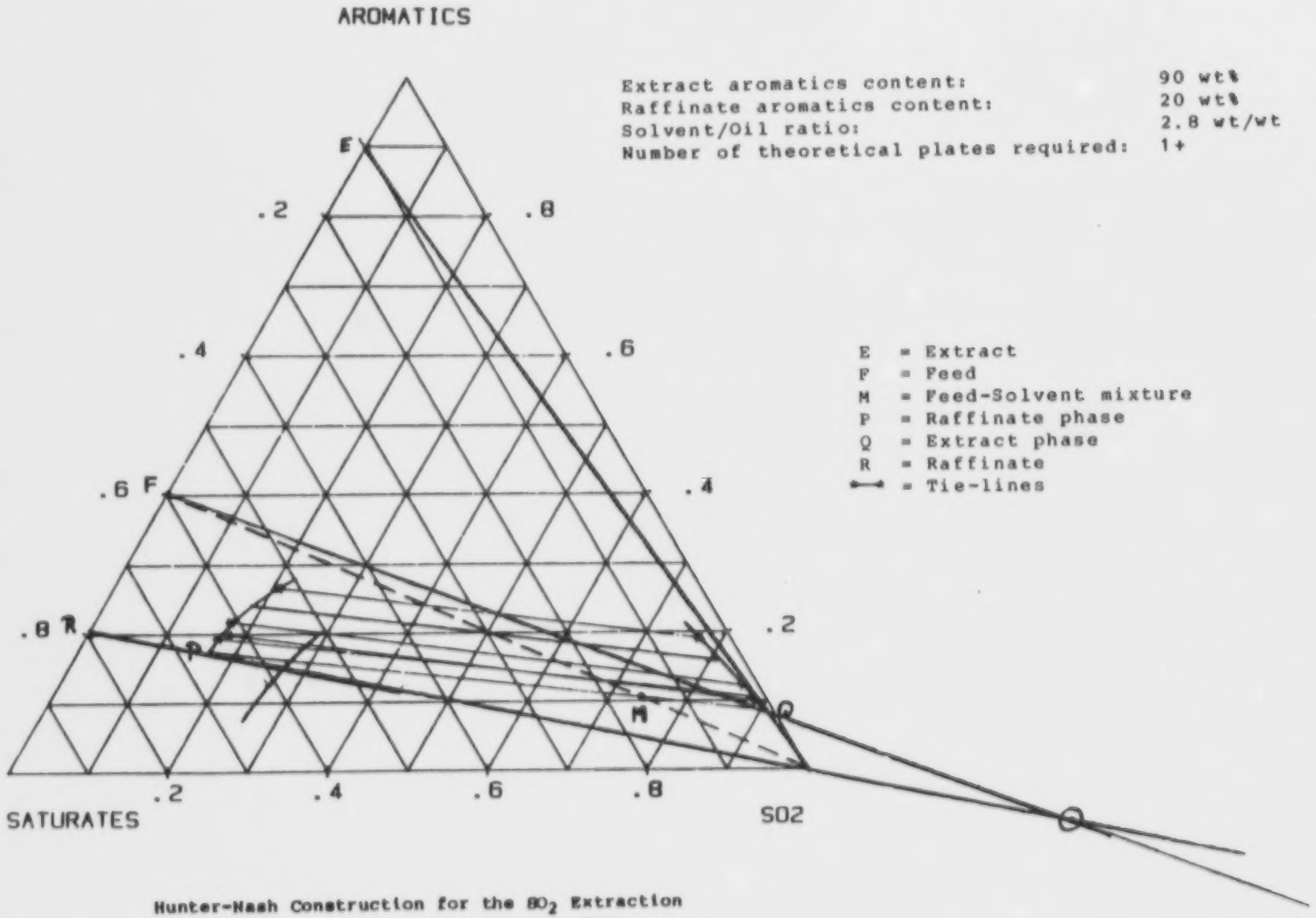


APPENDIX IV

Additional Process Design calculations (Hunter-Nash Constructions) pertaining to single-stage extractions of Syncrude and Suncor Middle Distillates. (These results have been discussed in Section 4.3.2).

FIGURE IV.1

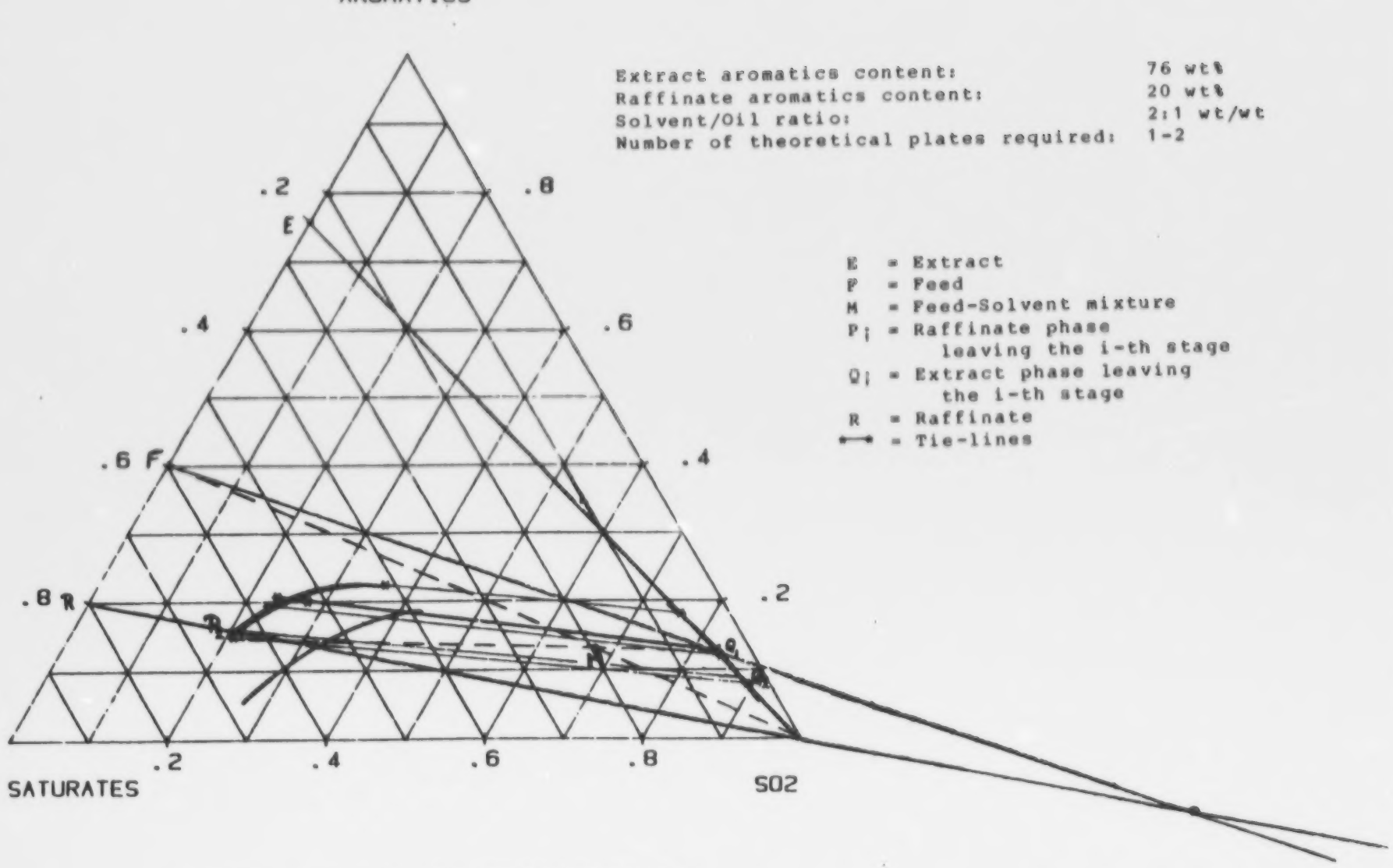
Process Design for Syncrude Middle Distillate
Extraction with SO_2 at -12°C



Hunter-Nash Construction for the SO_2 Extraction
of Syncrude Middle Distillate at -12°C

FIGURE IV.2

Process Design for Syncrude Middle Distillate
Extraction with SO_2 at 2°C

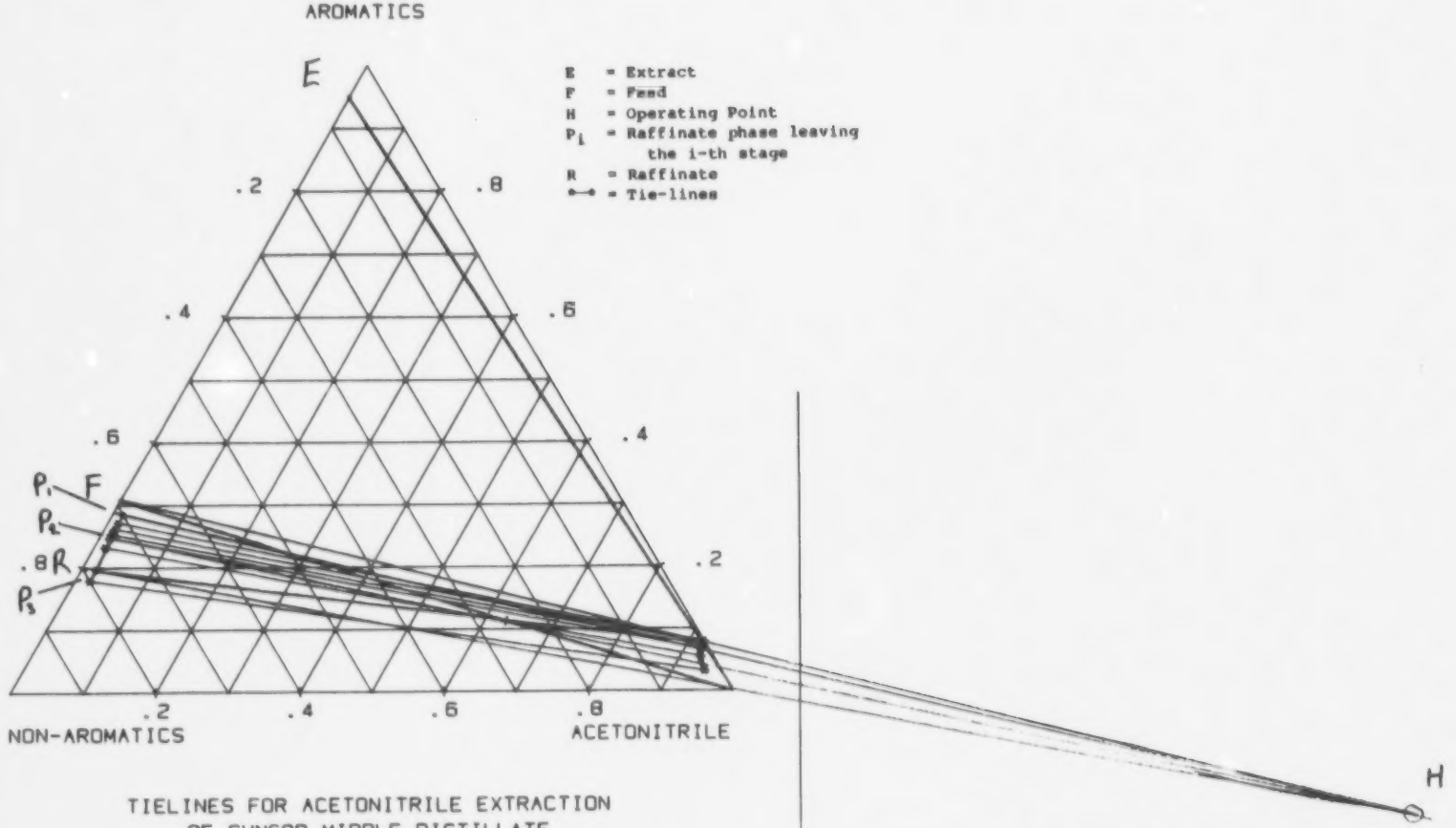


Hunter-Nash Construction for the SO_2 Extraction
of Syncrude Middle Distillate at 2°C

FIGURE IV.3

Process Design for Suncor
Middle Distillate Extraction with
Acetonitrile at 10°C

Extract aromatics content: 95 wt.%
Raffinate aromatics content: 20 wt.%
Solvent/Oil ratio: 1.7 wt/wt
Number of theoretical plates required: 2.5



TIELINES FOR ACETONITRILE EXTRACTION
OF SUNCOR MIDDLE DISTILLATE
AT (APPROXIMATELY) 10C

c

APPENDIX V

Additional Pilot Plant Data on Acetonitrile Extraction of Syncrude and Suncor Middle Distillates

Table V.1 of this Appendix shows the results of pilot plant extractions that were more difficult to evaluate than the data of Table 4.21 (Section 4.4.1). The most frequent difficulty was that the raffinate and extract phase flow rates were not sufficiently stable, even after a line-out period. In any event, none of the experiments of Table V.1 yielded equally good separations as the best runs of Table 4.21; hence the latter were more important for process optimization.

TABLE V.1

Pilot Plant Acetonitrile Extractions of Syncrude and Suncor Middle Distillates
Additional Survey Run Experimental Data

Experiment Number	Temp. °C	Nominal Solvent/Oil Ratio vol/vol	Actual Solvent/Oil Ratio wt/wt	Nominal Feed Rate mL/h	Actual Feed Rate mL/h	Feed g	Solvent g	Raffinate Phase g	Raffinate Phase Density g/mL	Solvent Content of the Raffinate Phase vol.%	Aromatics Content of the Raffinate Hydrocarbons wt.%
Syncrude											
20-1	27	2.0	1.94	250	240	205.2	399.1	143.2	0.8461	0.8	22.17
20-2	14	2.0	1.89	250	245	207.2	392.3	154.5	0.8492	0.8	26.65
20-3	27	1.6	1.99	300	265	203.3	405.1	160.1	0.8486	1.4	26.81
20-5	20	2.0	1.94	200	230	176.7	342.3	186.2	0.8495	0.3	25.30
20-6	20	2.5	2.46	300	260	224.1	550.9	171.5	0.8474	0.1	23.93
20-7	20	2.5	2.47	200	200	172.4	425.0	134.9	0.8467	2.0	22.63
20-8	20	1.5	1.43	200	205	176.7	252.6	149.5	0.8501	0.2	27.24
20-10	30	1.5	1.48	300	300	1038.8	1538.6	788.7	0.8495	2.2	27.02
20-11	30	2.0	1.94	300	310	267.3	519.4	153.4	0.8475	0.3	23.94
20-13	30	1.5	1.48	200	200	172.4	255.8	126.3	0.8484	2.2	24.99
20-15	30	2.5	2.49	300	265	452.6	1125.4	275.3	0.8440	1.6	19.55
Suncor											
20-16	20	1.6	1.55	200	210	355.8	550.9	278.9	0.8407	2.0	20.43
20-18	20	1.7	1.65	300	285	242.6	401.4	204.5	0.8411	2.0	20.79
20-20	20	1.7	1.66	100	100	166.0	275.5	121.9	0.8414	2.0	20.15
20-21	20	1.6	1.60	100	100	83.4	133.8	67.8	0.8414	2.0	21.16

APPENDIX VI

Product Quality Requirements as Formulated under ASTM and CGSB Specifications

NATIONAL STANDARD OF CANADA

NORME NATIONALE DU CANADA

CAN2-3.6-M83

Supersedes/Remplace
CAN2-3.6-M81

Diesel Fuel

Combustible diesel

Standard Specification VI.1

Canadian General Standards Board
Office des normes générales du Canada

CGSB

TABLE 1 TABLEAU 1

		TYPE AA	TYPE A	TYPE B	Method Méthode ASTM
Flash Point Point d'éclair	°C, Min.	40	40	40	D 3828 D 93 (Note 4) (Remarque 4)
Cloud Point Point de trouble	°C, Max.	-48	-34	(Note 5) (Remarque 5)	D 2500
Pour Point Point d'écoulement	°C, Max.	-51	-39	(Note 5) (Remarque 5)	D 97 (Note 6) (Remarque 6)
Kinematic Viscosity at 40°C, mm2/s (cSt) (Note 7) Viscosité cinématique à 40°C, mm2/s (cSt) (Remarque 7)	Min. Max.	1.2 -	1.3 4.1	1.4 4.1	D 445
Distillation: 90% Recovered Récupéré à 90%	°C, Max.	290	315	360	D 86
Water and Sediment, % vol. Eau et sédiment, % en vol.	Max.	0.05	0.05	0.05	D 1796 (Note 8) (Remarque 8)
Total Acid Number Indice d'acide total	Max.	0.10	0.10	0.10	D 974
Sulphur, % mass (Note 9) Soufre, % en masse (Remarque 9)	Max.	0.2	0.5	0.7	D 1552 (Note 10) (Remarque 10)
Copper Corrosion 3 h at 100°C Corrosion du cuivre 3 h à 100°C	Max.	No./No 1	No./No 1	No./No 1	D 130
Carbon Residue (Ramsbottom), on 10% bottoms, % mass (Note 11) Résidue de carbone (Rambsbottom) sur 10% de résidus, % en masse (Remarque 11)	Max.	0.15	0.15	0.20	D 524
Ash, % mass Cendre, % en masse	Max.	0.01	0.01	0.01	D 482
Ignition Quality, Cetane No. (Note 12) Aptitude à l'allumage, indice de cétane (Remarque 12)	Min.	40	40	40	D 613

NOTES APPLICABLE TO DETAIL REQUIREMENTS IN TABLE I

Note 4 - In the event of a dispute ASTM D 93 shall be the referee test method.

Note 5 - With the increasing use of fuel containing flow improver additives, low temperature requirements based on cloud and pour point may no longer apply. In all cases appropriate flow properties shall be designed, using the 2-1/2% low end design temperature data to provide satisfactory low temperature performance for the intended use (par 5.2). When required by the purchaser, the supplier shall be prepared to report:

a. The 2-1/2% temperature to which the product is designed

b. The test method used

c. The test method results.

Note 6 - Modify par. 5.7 of ASTM D 97 to perform the bath changes at sample temperatures of 9°C, -6°C and then when the oil temperature is 27°C above the bath temperature.

Note 7 - The SI unit for kinematic viscosity is metre squared per second. The preferred multiple for fluids in this viscosity range is millimetre squared per second which is equivalent to the centistokes (ie. 1 mm2/s = 1 cSt).

Note 8 - The centrifuge tube specified in ASTM D 2273 shall be substituted for that in ASTM D 1796.

Note 9 - Sulphur content may be established by government regulations where the fuel is to be used, or shall be as required by contractual agreement.

Note 10 - Sulphur content of Types AA and A may be determined by ASTM D 1266 (Lamp Method).

Note 11 - Carbon Residue Determination shall be performed on the base fuel before the addition of any additives.

REMARQUES APPLICABLES AUX EXIGENCES PARTICULIÈRES DU TABLEAU I

Remarque 4 - En cas de litige, la méthode D 93 de l'ASTM fera foi.

Remarque 5 - Compte tenu de l'utilisation accrue des combustibles contenant des additifs pour améliorer les propriétés d'écoulement, il n'est plus possible d'utiliser le point de trouble et le point d'écoulement pour déterminer les caractéristiques à basse température. Dans tous les cas, les propriétés d'écoulement appropriées doivent être établies à l'aide de la température de calcul minimale à 2-1/2% de façon à obtenir un rendement satisfaisant à basse température pour l'utilisation prévue (par. 5.2). Sur demande de l'acheteur, le fournisseur doit être prêt à indiquer:

a. La température de calcul à 2-1/2% du produit

b. La méthode d'essai utilisée

c. Les résultats des essais.

Remarque 6 - Modifier le par. 5.7 de D 97 de l'ASTM afin d'effectuer les changements de bain aux températures d'échantillonnage de 9°C, de -6°C et lorsque la température de l'huile dépasse de 27°C la température du bain.

Remarque 7 - Selon le Système International, la viscosité doit être exprimée en millimètres carrés par seconde, mais afin d'assurer la clarté, l'industrie du pétrole a décidé de garder cSt. Ces deux unités sont équivalentes (i.e., 1 mm2/s = 1 cSt).

Remarque 8 - Le tube centrifuge prescrit dans D 2273 de l'ASTM doit être remplacé par celui de D 1796 de l'ASTM.

Remarque 9 - La teneur en soufre peut être déterminée par un règlement gouvernemental en vigueur à l'endroit où le combustible doit être utilisé ou encore suivant une entente conclue entre les parties contractantes.

Remarque 10 - La teneur en soufre des combustibles de types AA et A peut être déterminée à l'aide de D 1266 de l'ASTM (méthode de la lampe).

Remarque 11 - La détermination du résidu de carbone doit se faire sur le combustible de base, avant qu'on y ajoute n'importe quel additif.

Note 12 - The calculated cetane index (ASTM D 976) or other calculated techniques that approximates cetane number (ASTM D 613) may be used for control purposes provided the buyer and seller agree.

A calculated technique shall not be used for determining the ignition quality of fuels containing cetane improvers. ASTM D 613 shall be used as the referee test method in the event of dispute.

Remarque 12 - L'indice de cétane calculé (ASTM D 976) ou d'autres techniques calculées qui se rapprochent de l'indice de cétane (ASTM D 613) peuvent être utilisées aux fins de contrôle pourvu qu'il y a entente entre l'acheteur et le vendeur.

Une technique calculée ne doit pas être utilisée pour déterminer l'aptitude à l'allumage des combustibles contenant des additifs destinés à améliorer l'indice de cétane. En cas de litige, la méthode d'essai D 613 de l'ASTM fera foi.

3. CLASSIFICATION

3.1 The fuels shall be supplied in the following grades with properties as specified in section 5:

Jet A
Jet A-1
Jet A-2.

CLASSIFICATION

Les carburants doivent être fournis dans les classes suivantes et avoir les propriétés prescrites à la section 5:

Jet A
Jet A-1
Jet A-2.

4. GENERAL REQUIREMENTS

4.1 The fuel shall be clear and free from undissolved water, sediment and suspended matter.

4.2 The odor of the fuel shall not be nauseating or irritating.

4.3 No substance known to be dangerously toxic under usual conditions of handling and use shall be present (except as specified herein).

EXIGENCES GÉNÉRALES

Le carburant doit être limpide, exempt d'eau non dissoute, de sédiments et de matière en suspension.

Le carburant ne doit pas dégager d'odeur nauséabonde ou irritante.

Le carburant doit être exempt de substances réputées toxiques dans les conditions habituelles de manutention et d'utilisation (sauf prescription de la présente norme).

5. DETAIL REQUIREMENTS

The fuels shall comply with the requirements below, *the limits of which are absolute and not subject to correction for tolerances of test methods.*

EXIGENCES PARTICULIÈRES

Le carburant doit être conforme aux exigences suivantes dont *les valeurs limites sont absolues et ne peuvent être corrigées pour tenir compte des tolérances des méthodes d'essai.*

		Jet A		Jet A-1		Jet A-2		Test Method	
		Min.	Max.	Min.	Max.	Min.	Max.	Méthode d'essai	
5.1	Flash Point, °C	38	--	38	--	33	--	ASTM D 56 or/ou D 3243	Point d'éclair, °C
5.2	Freezing Point, °C (Note 1)								Point de congélation, °C (Remarque 1)
	Summer (May 1 – Oct. 31)	--	−40 (Note/ Remarque 2)	--	−47	--	−40	ASTM D 2386	Été (1er mai – 31 octobre)
	Winter (Nov. 1 – Apr. 30)	N/A		--	−47	--	−47		Hiver (1er novembre – 30 avril)

		Jet A, Jet A-1 and/et Jet A-2 Min.	Max.	Test Method Méthode d'essai	
5.3	Kinematic Viscosity at −20°C (mm^2/s) (Note 3)	--	8	ASTM D 445	Viscosité cinématique à −20°C (mm^2/s) (Remarque 3)
5.4	Distillation			ASTM D 86	Distillation
5.4.1	10% Recovered Point, °C	--	204		Après distillation de 10%, °C
5.4.2	50% Recovered Point, °C	Report/Indiquer			Après distillation de 50%, °C
5.4.3	90% Recovered Point, °C	Report/Indiquer			Après distillation de 90%, °C
5.4.4	Final Boiling Point, °C	--	300		Point d'ébullition final, °C
5.4.5	Distillation Residue, % vol	--	1.5		Résidu de distillation, % en vol.
5.4.6	Distillation Loss, % vol	--	1.5		Perte à la distillation, % en vol.
5.5	Density, kg/m^3 at 15°C	774	839	ASTM D 1298	Masse volumique, kg/m^3 à 15°C
5.6	Sulfur, % mass	--	0.2	ASTM D 1266 or/ou D 2622 (Note/ Remarque 4)	Soufre, % en masse
5.7	Sulfur, Mercaptan, % mass (Note 5)	--	0.003	ASTM D 3227	Soufre, Mercaptan, % en masse (Remarque 5)
5.8	Corrosion (Copper Strip-Bomb) 2 h at 100°C	--	No./Nº 1	ASTM D 130	Corrosion (lame en cuivre-bombe) 2 h à 100°C
5.9	Corrosion (Silver Strip) (Note 6)	--	No./Nº 1	IP 227	Corrosion (lame d'argent) (Remarque 6)
5.10	Copper Content, mg/L (Note 7)	--	0.15	3-GP-0/131.1	Teneur en cuivre, mg/L (Remarque 7)
5.11	Water Separation Index (Modified)	75	--	ASTM D 2550 or/ou D 3602 or/ou D 3948	Indice de séparation d'eau (modifié)
5.12	Water Reaction Separation rating Interface rating	 -- --	 2 1 b	ASTM D 1094	Réaction à l'eau Indice de séparation Indice interfacial

		Jet A, Jet A-1 and/et Jet A-2 Min.	Max.	Test Method Méthode d'essai	
5.13	Net Heat of Combustion (Lower Heat Value), MJ/kg	42.8	--	ASTM D 1405 or/ou D 2382 (Note/ Remarque 8)	Chaleur nette de combustion (valeur minimale), MJ/kg
5.14	Aromatics, % vol (Note 9)	--	22.0	ASTM D 1319	Aromatique, % en vol. (Remarque 9)
5.15	Combustion Properties One of the following:				Propriétés de combustion. Une des suivantes:
	a. Luminometer number (Note 10)	45	--	ASTM D 1740	a. Indice photométrique. (Remarque 10)
	b. Smoke Point, mm	25	--	ASTM D 1322	b. Point de fumée, mm
	c. Smoke Point, mm, plus Naphthalenes, % vol (Note 11)	20 --	-- 3	ASTM D 1322 ASTM D 1840	c. Point de fumée, mm, plus naphthalènes, % en vol. (Remarque 11)
5.16	Total Acidity, mg KOH/g	--	0.1	ASTM D 974	Acidité totale, mg KOH/g
5.17	Particulate Matter, mg/L, at time of delivery to:			ASTM D 2276 (Note/ Remarque 12)	Particules, mg/L, lors de la livraison aux:
	a. Aircraft and refuellers	--	0.44		a. Aéronefs et camions-citernes
	b. Purchasers storage	--	2.2		b. Entrepôts de l'acheteur
5.18	Electrical Conductivity, pS/m at point, time and temperature of delivery to purchaser (par. 5.20.5)	50	450	ASTM D 2624	Conductivité électrique, pS/m, à l'endroit, au moment et à la température de la livraison à l'acheteur (al. 5.20.5)

Note 1	The freezing point limits shall be subject to review before June 30, 1983.
Note 2	Jet A – Suitable for summer (May 1 – October 31) use without operational restrictions.
Note 3	The SI unit for kinematic viscosity is meters squared per second. The preferred multiple for fluids in this viscosity range is millimetre squared per second which is equivalent to the centistokes (i.e., 1 mm^2/s = 1 cSt).
Note 4	ASTM D 1266 shall be the referee test in disputes.
Note 5	The mercaptan sulfur determination may be waived if the fuel is considered "sweet" by the Doctor Test described in section 4.2 of Specifications ASTM D 484, for Hydrocarbon Drycleaning Solvents.
Note 6	Purchasers Option
Note 7	The Copper Content requirement will be waived for fuels not subject to the "Copper Sweetening" process.
Note 8	ASTM D 2382 shall be the referee test in disputes.
Note 9	Fuel having an aromatics content over 22% by volume, but not exceeding 25% by volume is permitted, provided the supplier notifies the purchaser or at airports where comingled systems exist notifies the Chairman of the Airport Fuel Handling Committee of the volume, destination, and aromatic content within 30 d of such shipment.
Note 10	Fuel having a Luminometer Number less than 45 but not less than 40 is permitted provided the supplier notifies the purchaser or at airports where comingled systems exist notifies the Chairman of the Airport Fuel Handling Committee of the volume, destination, and Luminometer Number within 30 d of such shipment.
Note 11	Fuel having a smoke point less than 20 mm but not less than 18 mm and a naphthalenes content not exceeding 3% is permitted, provided the supplier notifies the purchaser or at airports where comingled systems exist notifies the Chairman of the Airport Fuel Handling Committee of the volume, destination, smoke point, and naphthalenes content within 30 d of such shipment.
Note 12	A minimum of 4 L shall be filtered.

Remarque 1	Les limites du point de congélation doivent faire l'objet d'une révision avant le 30 juin 1983.
Remarque 2	Jet A – Efficace en été (1er mai – 31 octobre) sans restrictions opérationnelles.
Remarque 3	D'après le Système International, la viscosité cinématique doit être exprimée en mètres carrés par seconde. En ce qui concerne la présente gamme de viscosité des fluides, le multiple recommandé est le millimètre carré par seconde qui équivaut au centistokes (i.e., 1 mm^2/s = 1 cSt).
Remarque 4	En cas de contestation, la méthode D 1266 de l'ASTM fera foi.
Remarque 5	Le dosage du soufre mercaptanique peut être exclu si le carburant est réputé "adouci" conformément à l'essai Doctor décrit à la section 4.2 de la méthode D 484 de l'ASTM et prescrit pour les solvants aux hydrocarbures employés dans le nettoyage à sec.
Remarque 6	Option de l'acheteur.
Remarque 7	L'exigence relative à la teneur en cuivre ne s'appliquera pas aux carburants qui ne sont pas soumis au procédé d'adoucissement au chlorure de cuivre.
Remarque 8	En cas de contestation, la méthode D 2382 de l'ASTM fera foi.
Remarque 9	Un carburant ayant une teneur en aromatiques supérieure à 22% en volume, mais ne dépassant pas 25% en volume, est permis, pourvu que le fournisseur avertisse l'acheteur – à l'aéroport où existent des systèmes mélangés, il faut avertir le président du comité de manutention des carburants – du volume, de la destination et de la teneur en aromatiques, dans un délai de 30 d à partir du moment de l'expédition.
Remarque 10	Un carburant ayant un indice photométrique inférieur à 45, sans jamais être inférieur à 40, est permis, pourvu que le fournisseur avertisse l'acheteur – à l'aéroport où existent des systèmes mélangés, il faut avertir le président du comité de manutention des carburants – du volume, de la destination et de l'indice photométrique, dans un délai de 30 d à partir du moment de l'expédition.
Remarque 11	Un carburant ayant un point de fumée inférieur à 20 mm, sans jamais être inférieur à 18 mm, et une teneur en naphthalènes ne dépassant pas 3%, est permis, pourvu que le fournisseur avertisse l'acheteur – à l'aéroport où existent des systèmes mélangés, il faut avertir le président du comité de manutention des carburants – du volume, de la destination, du point de fumée et de la teneur en naphthalènes, dans un délai de 30 d à partir du moment de l'expédition.
Remarque 12	Une quantité minimale de 4 L doit être filtrée.

5.19 **Thermal Stability** — The thermal stability shall be measured using either of the methods described in par. 5.19.1 or 5.19.2. It is anticipated that the Alcor JFTOT will eventually replace the ASTM-CRC Fuel Coker. Meanwhile both tests should be reported whenever possible. *(At present ASTM D 1660 will be the referee test method in the event of dispute).*

5.19.1 *ASTM-CRC Fuel Coker* — The change in pressure drop across the filter shall not exceed 10 kPa and the preheater deposit shall rate less than 3 when tested in accordance with ASTM D 1660, subject to the following conditions:

Preheater temperature	149 ± 3°C
Filter temperature	204 ± 6°C
Fuel flow	2.7 ± 0.05 kg/h
Test time	300 min

5.19.2 *Alcor Jet Fuel Thermal Oxidation Tester (JFTOT)* — The pressure drop across the filter shall not exceed 3.4 kPa and the heater tube deposit visual rating shall be less than 3 (blue or grey deposits shall be cause for rejection) when tested in accordance with ASTM D 3241 and subject to the following conditions:

Maximum heater tube temperature	260°C
Fuel system pressure	3.45 MPa
Fuel flow rate	3 mL/min
Test time	150 min

Testing facilities equipped with Mark 8A tube deposit rater should record and report spun ratings as well as visual ratings.

5.20 **Additives**

5.20.1 *Antioxidants* — To prevent gum formation the following antioxidants may be added, separately or in combination, to the fuel, the total concentration (not including weight of solvent) not to exceed 25 mg/L.

a. N, N'-disecondary butyl paraphenylenediamine
b. 2, 6-ditertiary butyl 4-methylphenol
c. 2, 4-dimethyl 6-tertiary butylphenol
d. 2, 6-ditertiary-butylphenol
e. N, N'-di-isopropyl paraphenylenediamine

Stabilité thermique — La stabilité thermique doit être mesurée à l'aide de l'une des méthodes décrites aux al. 5.19.1 ou 5.19.2. Il est prévu que le JFTOT Alcor remplacera éventuellement l'ASTM-CRC Fuel Coker. D'ici là, il faut présenter un rapport sur les deux essais lorsque cela est possible. *(À l'heure actuelle, la méthode d'essai D 1660 de l'ASTM fait foi en cas de contestation).*

ASTM-CRC Fuel Coker — Les variations de chute de pression dans tout le filtre ne doivent pas dépasser 10 kPa et l'évaluation du dépôt dans le préchauffeur doit être inférieure à 3 à l'essai de D 1660 de l'ASTM dans les conditions suivantes:

Température du préchauffeur	149 ± 3°C
Température du filtre	204 ± 6°C
Débit du carburant	2.7 ± 0.05 kg/h
Durée de l'essai	300 min

Appareil Alcor pour l'essai d'oxydation thermique des carburéacteurs (JFTOT) — La chute de pression dans tout le filtre ne doit pas dépasser 3.4 kPa et l'évaluation à vue du dépôt dans le tube du réchauffeur doit être inférieur à 3 (des dépôts bleus et gris entraînant l'annulation) à l'essai de D 3241 de l'ASTM dans les conditions suivantes:

Température maximale du tube du réchauffeur	260°C
Pression effective du dispositif d'alimentation en carburant	3.45 MPa
Débit du carburant	3 mL/min
Durée de l'essai	150 min

Les installations d'essai pourvues d'un déposimètre 8A doivent enregistrer et faire état des indications du déposimètre comme des évaluations visuelles.

Additifs

Antioxydants — Les antioxydants suivants peuvent être ajoutés séparément ou en combinaison au carburant; afin d'empêcher la formation de gommes, la concentration totale (excluant la masse du solvant) doit être d'au plus 25 mg/L.

a. N, N'- di-sec-butyl-p-phénylènediamine
b. 2, 6-di-tert-butyl-4-méthylphénol
c. 2, 4-diméthyl-6-tert-butylphénol
d. 2, 6-di-tert-butylphénol
e. N, N'-di-isopropyl-p-phénylènediamine

f. 75% minimum 2, 6-ditertiary-butylphenol
25% maximum tertiary and tritertiary butylphenols

g. 55% minimum 2, 4-dimethyl 6-tertiary butylphenol
45% maximum mixed tertiary and ditertiary butylphenols.

h. 60% minimum, 2,4-ditertiary butylphenol
40% maximum mixture of tertiary butylphenols.

When antioxidant is added to the fuel, the supplier shall state to the purchaser, on test certificates for material on import or manufacture, the amount and name of the antioxidant added to the fuel.

5.20.2 *Corrosion Inhibitors* — When specified (par. 7.1) a corrosion inhibitor approved by the purchaser shall be added to the fuel. When corrosion inhibitor is included in the fuel, the supplier shall state to the purchaser, on test certificates for material on import or manufacture, the amount and name of the inhibitor added.

5.20.3 *Metal Deactivator* — The following approved metal deactivator may be added to the fuel at a concentration not exceeding 5.7 mg/L: N,N' — disalicylidene — 1, 2-propane diamine. When metal deactivator is included in the fuel, the supplier shall state to the purchaser, on test certificates for material on import or manufacture, the amount of the specified deactivator added to the fuel.

5.20.4 *Fuel System Icing Inhibitor* — When requested (Par. 7.1) fuel system icing inhibitor conforming to latest version of 3-GP-526 shall be added to the fuel. The concentration at point of delivery shall be 0.10 to 0.15% volume as determined by 3-GP-0, Method 132.1.

5.20.5 *Static Dissipator Additive* — Static dissipator additive shall be added to the fuel to meet the electrical conductivity requirements of par. 5.16. The only approved static dissipator additive for aviation fuels is Shell ASA-3 (or ASA-350). Electrical conductivity varies with temperature. A typical relationship is

$$\log k_t = a\,(t - t_1) + \log k_{t1}$$

where k_t = electrical conductivity at temperature t, °C

k_{t1} = electrical conductivity at temperature t_1, °C

a = a factor which depends on fuel composition but normally is within the range 0.009 — 0.018.

f. au moins 75% de 2,6-di-tert-butylphénol
au plus 25% de tert-butylphénol et de tri-tert-butylphénol

g. au moins 55% de 2,4-diméthyl-6-tert-butylphénol
au plus 45% d'un mélange constitué de tert-butylphénol et de di-tert-butylphénol

h. au moins 60% de 2,4-di-tert-butylphénol
au plus 40% d'un mélange de tert-butylphénols.

Lorsqu'un antioxydant est ajouté au carburant, le fournisseur doit déclarer à l'acheteur, sur les certificats d'essai des produits importés ou fabriqués, la quantité et la désignation de l'antioxydant ajouté.

Inhibiteurs de corrosion — Lorsqu'il est prescrit (par. 7.1), un inhibiteur de corrosion approuvé par l'acheteur doit être ajouté au carburant. Lorsqu'un inhibiteur de corrosion est incorporé au carburant, le fournisseur doit déclarer à l'acheteur, sur les certificats d'essai des produits importés ou fabriqués, la quantité et la désignation de l'inhibiteur ajouté.

Désactiveur de métaux — Le désactivateur de métaux ayréé ci-après peut être ajouté au carburant à une concentration d'au plus 5.7 mg/L: N,N'-disalicylidène-1,2-diaminopropane. Lorsqu'un désactiveur de métaux a été ajouté au carburant, le fournisseur doit déclarer à l'acheteur, sur les certificats d'essai des produits importés ou fabriqués, la quantité de désactiveur prescrit ajouté au carburant.

Inhibiteur antigel du système d'alimentation en carburant — Lorsqu'il est prescrit (par. 7.1), un inhibiteur antigel conforme aux exigences de la dernière édition de la norme 3-GP-526 doit être incorporé au carburant. Le volume de concentration, au moment de la livraison, doit être de 0.10 à 0.15%, conformément à la méthode 132.1 de la norme 3-GP-0.

Additif antistatique — Un additif antistatique doit être incorporé au carburant pour satisfaire aux exigences relatives à la conductivité électrique prescrites au par. 5.18. Le seul additif antistatique approuvé pour les carburants d'aviation est le Shell ASA-3 (ou ASA-350). La conductivité électrique varie selon la température. Voici un rapport type température/conductivité:

$$\log k_t = a\,(t - t_1) + \log k_{t1}$$

où k_t = conductivité électrique à la température t, °C

k_{t1} = conductivité électrique à la température t_1, °C

a = facteur variant selon la composition du carburant, mais habituellement compris dans la plage 0.009 — 0.018.

Designation: D 1655 – 85a

Standard Specification VI.3

Standard Specification for AVIATION TURBINE FUELS[1]

This standard is issued under the fixed designation D 1655; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This specification is for the use of purchasing agencies in formulating specifications for purchases of aviation turbine fuel under contract.

1.2 This specification defines specific types of aviation turbine fuel for civil use. It does not include all fuels satisfactory for aviation turbine engines. Certain equipment or conditions of use may permit a wider, or require a narrower, range of characteristics than is shown by this specification.

2. Applicable Documents

2.1 *ASTM Standards:*

D56 Test Method for Flash Point by Tag Closed Tester[2]

D86 Method for Distillation of Petroleum Products[2]

D130 Test Method for Detection of Copper Corrosion from Petroleum Products by the Copper Strip Tarnish Test[2]

D235 Specification for Petroleum Spirits (Mineral Spirits)[2]

D240 Test Method for Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Method[2]

D323 Test Method for Vapor Pressure of Petroleum Products (Reid Method)[2]

D381 Test Method for Existent Gum in Fuels by Jet Evaporation[2]

D445 Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and Calculation of Dynamic Viscosity)[2]

D873 Test Method for Oxidation Stability of Aviation Fuels (Potential Residue Method)[2]

D974 Test Method for Neutralization Number by Color-Indicator Titration[2]

D1094 Test Method for Water Reaction of Aviation Fuels[2]

D1266 Test Method for Sulfur in Petroleum Products (Lamp Method)[2]

D1298 Test Method for Density, Relative Density, or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method[2]

D1319 Test Method for Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption[2]

D1322 Test Method for Smoke Point of Aviation Turbine Fuels[2]

D1405 Method for Estimation of Net Heat of Combustion of Aviation Fuels[2]

D1552 Test Method for Sulfur in Petroleum Products (High-Temperature Method)[2]

D1660 Test Method for Thermal Stability of Aviation Turbine Fuels[2]

D1740 Test Method for Luminometer Numbers of Aviation Turbine Fuels[3]

D1840 Test Method for Naphthalene Hydrocarbons in Aviation Turbine Fuels by Ultraviolet-Spectrophotometry[3]

D2276 Test Method for Particulate Contaminant in Aviation Turbine Fuels[3]

D2382 Test Method for Heat of Combustion of Hydrocarbon Fuels by Bomb Colorimeter (High Precision Method)[3]

D2386 Test Method for Freezing Point of Aviation Fuels[3]

D2550 Test Method for Water Separation Characteristics of Aviation Turbine Fuels[3]

D2622 Test Method for Sulfur in Petroleum Products (X-Ray Spectrographic Method)[3]

D2624 Test Method for Electrical Conductivity of Aviation Distillate Fuels Containing a Static Dissipator Additive[3]

D3227 Test Method for Mercaptan Sulfur in Gasoline, Kerosine, Aviation Turbine and Distillate Fuels (Potentiometric Method)[4]

D3240 Test Method for Lithium and Sodium in Lubricating Greases by Flame Photometer[4]

D3241 Test Method for Thermal Oxidation Stability of Aviation Turbine Fuels (JFTOT Procedure)[4]

D3242 Test Method for Total Acidity in Aviation Turbine Fuels[4]

D3338 Method for Estimation of Heat of Combustion of Aviation Fuels[4]

D3602 Standard Field Test for Water Separation Characteristics of Aviation Turbine Fuels[4]

D3828 Test Method for Flash Point by Setaflash Closed Tester[4]

D3830 Practice for Filter Membrane Color Ratings of Aviation Turbine Fuels[4]

D3948 Method for Determining Water-Separation Characteristics of Aviation Turbine Fuels by Portable Separometer[4]

D4052 Test Method for Density and Relative Density of Liquids by Digital Density Meter[4]

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products[4]

D4171 Specification for Fuel System Icing Inhibitors[4]

D4176 Test Method for Free Water and Particulate Contamination in Distillate Fuels (Clear and Bright Pass/Fail Procedures)[4]

D4306 Practice for Sampling Aviation Fuel for Tests Affected by Trace Contamination[4]

D4308 Test Method for Electrical Conductivity of Liquid Hydrocarbons by Precision Meter[4]

3. General

3.1 This specification, unless otherwise provided, prescribes the required properties of aviation turbine fuel at the time and place of delivery.

4. Types

4.1 Three types of aviation turbine fuels are provided, as follows:

4.1.1 *Jet A and Jet A-1*—A relatively high flash point distillate of the kerosine type.

4.1.2 *Jet B*—A relatively wide boiling range volatile distillate.

4.2 Jet A and Jet A-1 represent two grades of kerosine fuel that differ in freezing point. Other grades would be suitably identified.

5. Materials

5.1 Aviation turbine fuel, except as otherwise specified herein, shall consist of blends of refined hydrocarbons derived from crude petroleum, natural gasoline, or blends thereof with synthetic hydrocarbons.

5.2 *Additives* may be added to each type of aviation turbine fuel in the amount and of the composition specified in the following list of approved material:[5]

5.2.1 *Antioxidants* in amount not to exceed 8.4 lb (not including weight of solvent) per 1000 bbl (42 gal) (24.0 mg/L):

5.2.1.1 *N,N*-diisopropylparaphenylene diamine.

5.2.1.2 75 % min 2,6-ditertiary-butyl phenol plus 25 % max tertiary and tritertiary butyl phenols.

5.2.1.3 72 % min 2,4-dimethyl-6-tertiary-butyl phenol plus 28 % max monomethyl and dimethyl tertiary-butyl phenols.

5.2.1.4 55 % min 2,4-dimethyl-6-tertiary-butyl phenol plus 45 % max mixed tertiary and ditertiary butyl phenols.

5.2.2 *Metal Deactivator*, in amount not to exceed 2.0 lb (not including weight of solvent) per 1000 bbl (42 gal) (5.7 mg/L):

5.2.2.1 *N,N*-disalicylidene-1,2-propane diamine.

5.2.3 Other additives are permitted under 5.1 and Section 7. These include electrical conductivity additives, fuel system icing inhibitor, other antioxidants, inhibitors, and special-purpose additives. The quantities and types must be declared by the manufacturer and agreed to by the purchaser.

5.2.3.1 *Electrical Conductivity Additives*[6] ASA-3[6] in concentrations up to 1 mg/L and "Stadis" 450[7] in concentrations up to 3 mg/L are permitted.

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[1] This specification is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.J on Aviation Fuels.

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[2] *Annual Book of ASTM Standards*, Vol 05.01.

[3] *Annual Book of ASTM Standards*, Vol 05.02.

[4] *Annual Book of ASTM Standards*, Vol 05.03.

[5] Guidelines for Approval or Disapproval of Additives are available from ASTM, 1916 Race St., Philadelphia, PA 19103 as RR: D02-1125.

[6] Shell ASA-3 is marketed by Royal Lubricants Corp., Roseland, NJ 07068.

[7] Stadis 450 is marketed by DuPont Petroleum Chemicals Div., Wilmington, DE 19898.

5.2.3.2 *Fuel System Icing Inhibitor:*

5.2.3.2(a) *Ethylene Glycol Monomethyl Ether*, conforming to the requirements of Specification D 4171, may be used in concentration of 0.1 to 0.15 volume %. **(Danger)**—EGME (2-methoxyethanol) is hazardous. Avoid skin and eye contact and inhalation of its vapors to avoid possible adverse health effects. Consult your suppliers' safety data sheet.)

6. Detailed Requirements

6.1 The aviation turbine fuel shall conform to the requirements prescribed in Table 1.

7. Workmanship

7.1 The aviation turbine fuel herein specified shall be visually free of undissolved water, sediment, and suspended matter. The odor of the fuel shall not be nauseating or irritating. No substance of known dangerous toxicity under usual conditions of handling and use shall be present, except as permitted herein.

8. Sampling

8.1 Because of the importance of proper sampling procedures in establishing fuel quality, use the appropriate procedures in Practice D 4057.

8.2 A number of jet fuel properties including thermal stability, water separation, electrical conductivity, and others are very sensitive to trace contamination which can originate from sample containers. For recommended sample containers refer to Practice D 4306.

9. Report

9.1 The type and number of reports to ensure conformance with the requirements of this specification shall be mutually agreed upon by the seller and the purchaser of the aviation turbine fuel.

10. Test Methods

10.1 The requirements enumerated in this specification shall be determined in accordance with the following ASTM test methods.

10.1.1 *Gravity*—Test Method D 1298 or Test Method D 4052.

10.1.2 *Distillation*—Method D 86.

10.1.3 *Vapor Pressure*—Test Method D 323.

10.1.4 *Flash Point*—Test Method D 56 or Test Method D 3828.

10.1.5 *Freezing Point*—Test Method D 2386.

10.1.6 *Viscosity*—Test Method D 445.

10.1.7 *Net Heat of Combustion*—Method D 1405, Test Method D 3338, or Test Method D 2382.

10.1.8 *Corrosion (Copper Strip)*—Test Method D 130.

10.1.9 *Total Acidity*—Test Method D 974 or Test Method D 3242.

10.1.10 *Sulfur*—Test Method D 1266, Test Method D 1552, or Test Method D 2622.

10.1.11 *Mercaptan Sulfur*—Test Method D 3227.

10.1.12 *Water Reaction*—Test Method D 1094.

10.1.13 *Existent Gum*—Test Method D 381.

10.1.14 *Thermal Stability*—Test Method D 1660 or Test Method D 3241.

NOTE—In Table 1, Test Method D 3241 is accepted as an alternate method of test to Test Method D 1660 if the test temperatures are selected first at 260°C and subsequently at 245°C if the requirements are not met first at the higher temperature. This two-tier testing sequence is intended to promote familiarization with the Test Method D 3241 equipment and to span the temperature considered to provide product quality equivalent to that provided by Test Method D 1660 at 300°F/400°F/6 lb/h. It is intended to establish a single JFTOT test temperature when data are sufficient to make the decision.

10.1.15 *Aromatics*—Test Method D 1319.

10.1.16 *Smoke Point*—Test Method D 1322.

10.1.17 *Luminometer Number*—Test Method D 1740.

10.1.18 *Naphthalene Content*—Test Method D 1840.

10.1.19 *Electrical Conductivity*—Test Method D 2624 or Test Method D 4308.

D 1655

TABLE 1 Detailed Requirements of Aviation Turbine Fuels[A]

Property	Jet A or Jet A-1	Jet B	ASTM Test Method[B]
Acidity, total max, mg KOH/g	0.1	...	D 974 or D 3242
Aromatics, vol, max, %	20[C]	20[C]	D 1319
Sulfur, mercaptan,[D] wt, max, %	0.003	0.003	D 3227
Sulfur, total wt, max, %	0.3	0.3	D 1266 or D 1552 or D 2622
Distillation temperature, °F (°C)			
10 % recovered, max, temp	400 (204.4)	...	D 86
20 % recovered, max, temp	...	290 (143.3)	
50 % recovered, max, temp	report	370 (187.8)	
90 % recovered, max, temp	report	470 (243.3)	
Final boiling point, max, °F (°C)	572 (300)		
Distillation residue, max, %	1.5	1.5	
Distillation loss, max, %	1.5	1.5	
Flash point, min, °F (°C)	100 (37.8)		D 56 or D 3828[E]
Gravity, max, °API (min, sp gr) at 60°F	51 (0.7753)	57 (0.7507)	D 1298 or D 4052
Gravity, min, °API (max, sp gr) at 60°F	37 (0.8398)	45 (0.8017)	D 1298 or D 4052
Vapor pressure, max, lb	...	3	D 323
Freezing point, max, °C	−40 Jet A[F] −47 Jet A-1[F,G]	−50[F]	D 2386
Viscosity −4°F (−20°C) max, cSt (mm^2/s^{-1})	8		D 445
Net heat of combustion, min, Btu/lb	18 400[H]	18 400[H]	D 1405 or D 2382, or D 3338
Combustion properties, one of the following requirements shall be met:			
(1) Luminometer number, min or	45	45	D 1740
(2) Smoke point, min (mm) or	25	25	D 1322
(3) Smoke point, min (mm) and	20[G]	20[G]	D 1322
Naphthalenes, vol, max (mm), %	3	3	D 1840
Corrosion, copper strip 2 h at 212°F (100°C) max	No. 1	No. 1	D 130
Thermal stability: one of the following requirements shall be met			
(1) Filter pressure drop, max, in. Hg	3	3	D 1660[I]
Preheater deposit less than	Code 3	Code 3	
(2) Filter pressure drop, max, mm Hg	25	25	D 3241[J]
Tube deposit less than	Code 3	Code 3	
Existent gum, max, mg/100 mL	7	7	D 381
Water reaction:			
Separation rating, max	(2)	(2)	D 1094
Interface rating, max	1b	1b	D 1094
Additives	See 5.2		
Electrical conductivity, pS/m	[K]	[K]	D 2624 or D 4308

[A] The requirements herein are absolute and are not subject to correction for tolerance of the test methods. If multiple determinations are made, average results shall be used.

[B] The test methods indicated in this table are referred to in Section 9.

[C] Fuels with an aromatic content over 20 volume % but not exceeding 25 volume % are permitted provided the supplier (seller) notifies the purchaser of the volume, distribution and aromatic content within 90 days of date of shipment unless other reporting conditions are agreed to by both parties.

[D] The mercaptan sulfur determination may be waived if the fuel is considered sweet by the doctor test described in 4.2 of Specification D 235.

[E] Other freezing points may be agreed upon between supplier and purchaser.

[F] The −47°C maximum freezing point limit for Jet A-1 is subject to reapproval in 1988. If not reapproved, the value will revert to −50°C maximum.

[G] Fuels having a smoke point less than 20 but not less than 18 and a maximum of 3 volume % of naphthalenes are permitted provided the supplier (seller) notifies the purchaser of the volume, distribution and smoke point and naphthalenes content within 90 days of date of shipment unless other reporting conditions are agreed to by both parties.

[H] Use for Jets A and A-1 the value calculated from Table 8 or Eqs 5 and 9 in Method D 1405. Use for Jet B the value calculated from Table 6 or Eqs 5 and 7 in Method D 1405. Test Methods D 2382 or D 3338 may be used as alternatives. In case of dispute Test Method D 2382 must be used.

[I] Thermal stability test shall be conducted for 5 h at 300°F (148.8°C) preheater temperature, 400°F (204.4°C) filter temperature, and at a flow rate of 6 lb/h.

[J] Thermal stability test (JFTOT) shall be conducted for 2.5 h at a control temperature of 260°C but if the requirements of Table 1 are not met, the test may be conducted for 2.5 h at a control temperature of 245°C. Results at both test temperatures shall be reported in this case. Tube deposits shall always be reported by the Visual Method a rating by the Tube Deposit Rating (TDR) optical density method is desirable but not mandatory.

[K] A limit of 50 to 450 conductivity units (pS/m) applies only when an electrical conductivity additive is used and under the condition at point of use.

TABLE 1 *Continued*

1 pS/m = 1×10^{-12} Ω^{-1} m^{-1}

[F] Results obtained by Test Method D 3828 may be up to 3°F (1.7°C) below those obtained by Test Method D 56 which is the preferred method. In case of dispute, Test Method D 56 will apply.

APPENDIXES

(Nonmandatory Information)

X1. PERFORMANCE CHARACTERISTICS OF AVIATION TURBINE FUELS

X1.1 Introduction

X1.1.1 In recent years the specifications for aviation turbine fuels have incorporated new test methods that are not described in ASTM STP 7C.[8] Up-to-date information on the significance of all methods is more readily available to users as an appendix to the specifications.

X1.2 Significance

X1.2.1 Specification D 1655 defines two types of jet fuel for civil use. Limiting values for the two types of fuel covered are placed on fuel properties believed to be related to the performance of the aircraft and engines in which they are most commonly used.

X1.2.2 The safe and economical operation of aircraft requires fuel that is essentially clean and dry and free of any contamination prior to use. It is possible to measure a number of jet fuel characteristics related to quality.

X1.2.3 The significance of standard tests for fuel properties may be summarized for convenience in terms of the technical relationships with performance characteristics as shown in Table X1.1.

X1.3 Thermal Stability

X1.3.1 Stability to oxidation and polymerization at the operating temperatures encountered in certain jet aircraft is an important performance requirement. The "thermal stability" measurements are related to the amount of deposits formed in the engine fuel system on heating the fuel in a jet aircraft. Commercial jet fuels should be thermally stable at fuel temperature as high as 300°F. Such fuels have been demonstrated to have inherent storage stability as previously measured by a test for potential residue (Test Method D 873).

X1.4 Combustion

X1.4.1 Jet fuels are continuously burned in a combustion chamber by injection of liquid fuel into the rapidly flowing stream of hot air. The fuel is vaporized and burned at near stoichiometric conditions in a primary zone. The hot gases so produced are continuously diluted with excess air to lower their temperature to a safe operating level for the turbine. Fuel combustion characteristics relating to soot formation are emphasized by current specification test methods. Other fuel combustion characteristics not covered in current specifications are burning efficiency and flame-out.

X1.4.2 In general, paraffin hydrocarbons offer the most desirable combustion cleanliness characteristics for jet fuels. Naphthenes are the next most desirable hydrocarbons for this use. Although olefins generally have good combustion characteristics, their poor gum stability usually limits their use in aircraft turbine fuels to about 1 % or less. Aromatics generally have the least desirable combustion characteristics for aircraft turbine fuel. In aircraft turbines they tend to burn with a smoky flame and release a greater proportion of their chemical energy as undesirable thermal radiation than the other hydrocarbons. Naphthalenes or bicyclic aromatics produce more soot, smoke, and thermal radiation than monocyclic aromatics and are, therefore, the least desirable hydrocarbon class for aircraft jet fuel use. All of the following measurements are influenced by the hydrocarbon composition of the fuel and, therefore, pertain to combustion quality: luminometer number, smoke point, percent naphthalenes, smoke-volatility index, and percent aromatics.

X1.4.2.1 *Luminometer Number*—This method covers measurement of the radiation from and temperature rise in a flame under prescribed conditions and is related to the hydrocarbon-type composition of such fuels.

X1.4.2.2 *Smoke Point*—This method provides an indication of the relative smoke-producing properties of jet fuels and is related to the hydrocarbon-type composition of such fuels. Generally, the more highly aromatic the jet fuel, the more smoky the flame. A high smoke point indicates a fuel of low smoke-producing tendency.

X1.4.2.3 *Aromatics*—The combustion of highly aromatic jet fuels generally results in smoke and carbon or soot deposition, and it is therefore desirable to limit the total aromatic content as well as the naphthalenes in jet fuels.

X1.4.2.4 *Percent Naphthalenes*—This method covers measurement of the total concentration of naphthalene, acenaphthene, and alkylated derivatives of these hydrocarbons in jet fuels containing no more than 5 % of such compounds and having boiling points below 600°F (316°C).

X1.5 Fuel Metering and Aircraft Range

X1.5.1 *Gravity, °API*—The API gravity is a property of a fluid and is of significance in metering flow and in weight-volume relationships for most commercial transactions. API gravity is related inversely to specific gravity. It is particularly useful in empirical assessments of heating value when used with other parameters such as aniline point. A high API or low specific gravity may indicate low heating value per unit volume.

X1.5.2 *Net Heat of Combustion*—The design of aircraft and engines is based on the convertibility of heat into mechanical energy. The net heat of combustion provides a knowledge of the amount of energy obtainable from a given fuel for the performance of useful work; in this instance, power. Aircraft design and operation are dependent upon the availability of a certain predetermined minimum amount of energy as heat. Consequently, a reduction in heat energy below this minimum is accompanied by an increase in fuel consumption with corresponding loss of range. Therefore, a minimum net heat of combustion requirement is incorporated in this specification. The determination of net heat of combustion is time consuming and difficult to conduct accurately. This led to the development and use of Method employing the aniline gravity product to estimate the net heat of combustion of the fuel. The aniline gravity product is obtained by multiplying the aniline point of the fuel in degrees Fahrenheit by the gravity in °API. It is used along with the sulfur content of the fuel to obtain the net heat of combustion for the purposes of this specification. An alternative calculation Method D 3338 is based on correlations of aromatics content, gravity, volatility, and sulfur content. This method may be preferred at refineries where all these values are normally obtained and the necessity to obtain the aniline point is avoided. The direct measurement method is normally used only as a referee method in cases of dispute.

X1.6 Fuel Atomization

X1.6.1 *Distillation*—The fuel volatility and ease of vaporization at different temperatures are determined by distillation. The 10 % distilled temperatures are limited to assure easy starting. The 90 % limit excludes heavier fractions that would be difficult to vaporize.

X1.6.2 *Vapor Pressure*—The Reid vapor pressure serves as a criterion of freedom from foaming, fuel slugging, and losses of light ends through aircraft tank vents at high altitude. This is of significance with respect of Jet B fuel because of its higher volatility.

X1.6.3 *Viscosity*—The viscosity of a fuel is closely related to pumpability over the temperature range and consistency of nozzle spray patterns. The ability of fuel to lubricate a pump may also be related to the viscosity.

X1.7 Fluidity at Low Temperatures

X1.7.1 *Freezing Point*—The freezing point is particularly important and must be sufficiently low to preclude interference with flow of fuel through filter screens to the engine at temperatures prevailing at high altitudes. The temperature of fuel in an aircraft tank decreases at a rate proportional to the duration of flight. The maximum freezing point allowed for the fuel is therefore related to the type of flight. For example, long duration flights would require fuel of lower freezing point than short duration flights.

X1.8 Compatibility with Elastomer and the Metals in the Fuel System and Turbine

X1.8.1 *Mercaptan Sulfur*—Mercaptans are known to be reactive with certain elastomers. A limitation in mercaptan content is specified to preclude such reactions and to minimize the unpleasant mercaptan odor.

X1.8.2 *Sulfur*—Control of sulfur content is significant for jet fuels because the sulfur oxides formed during combustion may be corrosive to turbine metal parts.

X1.8.3 *Copper Strip Corrosion*—A requirement that jet fuel must pass the copper strip test assures that the fuel will not corrode copper or any copper-base alloys in various parts of the fuel system.

X1.8.4 *Total Acidity*—Some petroleum products are treated with mineral acid or caustic, or both, as part of the refining procedure. Any residual mineral acid or caustic is undesirable. Neither impurity is likely to be present. However, a determination of acidity confirms this when inspecting new or unused fuel. It also measures organic acids if present.

X1.9 Fuel Storage Stability

X1.9.1 *Existent Gum*—Gum is a nonvolatile residue left on evaporation of fuel. A steam jet is used as an evaporating agent for fuels that are to be used in aircraft equipped with turbine engines. The amount of gum present is an indication of the condition of the fuel at the time of test only. Large quantities of gum are indicative of contamination of fuel by higher boiling oils or particulate matter and generally reflect poor fuel handling practices.

X1.9.2 *Potential Residue*—Fuel must be usable after storage for variable periods under a variety of climatic conditions. The potential residue test, which is an accelerated oxidation method, is used to estimate fuel stability in storage and the effectiveness of oxidation inhibitors. A 16-h oxidation period is specified so as to ensure stability during long periods under severe conditions such as extended storage in tropical climates. Test Method D 873 describes a suitable technique.

X1.10 Fuel Cleanliness and Handling

X1.10.1 *Flash Point*—The flash point is an indication of the maximum temperature for fuel handling and storage without serious fire hazard. The shipment, storage and handling precautions regulated by municipal, state, or federal laws and insurance requirements are a function of the flash point for the particular fuel being utilized.

X1.10.2 *Water Reaction*—The water reaction method provides a means of determining the presence of materials readily extractable by water or having a tendency to absorb water. When the fuel consists essentially of hydrocarbon components, there is no measurable change in the volume of the water layer.

X1.10.3 *Water Separation Characteristics*—The ease of coalescence of water from fuels as influenced by surface active agents (surfactants) is assessed by Test Method D 2550, Standard Field Test D 3602, or by Method D 3948. Test Method D 2550 is a laboratory method, whereas Standard Field Test D 3602 and Method D 3948 use smaller separometers suitable for field or laboratory use. A high rating suggests a fuel free of surfactants; a low rating indicates that surfactants

[8] *Significance of Tests for Petroleum Products*, ASTM STP 7C, ASTM, 1977.

are present. Surfactants, which may be contaminants or deliberately added materials, may gradually disarm filter coalescers, allowing fine water droplets and particulate contaminants to pass separators in ground handling equipment.

X1.10.4 *Free Water and Particulate Contamination in Distillate Fuels (Clear and Bright Pass/Fail Procedures)*—The procedures in Test Method D 4176 provide rapid but nonquantitative methods for detecting contamination in a distillate fuel. Other following methods permit quantitative determinations.

X1.10.5 *Particulate Matter*—The presence of adventitious solid particulate contaminants such as dirt and rust may be detected by filtration of the jet fuel through membrane filters under prescribed conditions. Test Method D 2276 describes a suitable technique.

X1.10.6 *Membrane Color Ratings*—Filtering the fuel through a membrane and rating the color of the deposits against a standard color scale offers a qualitative assessment of particulate contaminant levels in fuels or of changes in fuel contaminant levels at a particular location. Practice D 3830 describes a suitable technique.

X1.10.7 *Undissolved Water*—The test method for undissolved water provides a quantitative means for measuring the amount of undissolved or free water in flowing fuel streams without exposing the sample to the atmosphere or to a sample container. It also provides a means for checking the performance of fuel filter-separators. Test Method D 3240 describes this test method.

X1.11 Miscellaneous

X1.11.1 *Additives*—Antioxidants and metal deactivator are used to prevent the formation of oxidation deposits in aircraft engine fuel systems, to counteract the catalytic effects of active metals in fuel systems and to improve the oxidation stability of fuels in storage. Other additives are available to inhibit corrosion of steel in fuel systems, to improve the fuel lubricity, to increase the electrical conductivity of fuel, and to prevent the formation of ice in fuel systems containing water. The acceptability of additives for use must ultimately be determined by full-scale engine tests or flight trials. The chemical names of approved additives and the maximum quantities permitted are shown in the specifications.

X1.11.2 *Sample Containers*—A practice for sampling aviation fuel for tests affected by trace contamination can be found in Practice D 4306.

X1.11.1(a) *Fuel System Icing Inhibitor*, ethylene glycol monomethyl ether approved in 5.2.3.2 shall conform to the requirements shown in Specification D 4171.

TABLE X1.1 Performance Characteristics of Aviation Turbine Fuels

Performance Characteristics	Test Method	Sections
Engine fuel system deposits and coke	Thermal stability	X1.3
Combustion properties	Luminometer number	X1.4.1
	Smoke point	X1.4.2
	Aromatics	X1.4.3
	Percent naphthalenes	X1.4.4
Fuel metering and aircraft range	Gravity, API	X1.5.1
	Net heat of combustion	X1.5.2
Fuel atomization	Distillation	X1.6.1
	Vapor pressure	X1.6.2
	Viscosity	X1.6.3
Fluidity at low temperature	Freezing point	X1.7.1
Compatibility with elastomer and the metals in the fuel system and turbine	Mercaptan sulfur	X1.8.1
	Sulfur	X1.8.2
	Copper strip corrosion	X1.8.3
	Acidity	X1.8.4
Fuel storage stability	Existant gum	X1.9.1
	Potential residue	X1.9.2
Fuel cleanliness, handling	Flash point	X1.10.1
	Water reaction	X1.10.2
	Water separtion characteristics	X1.10.3
	Free water and particulate contamination D 4176	X1.10.4
	Particulate matter	X1.10.5
	Membrane color ratings D 3830	X1.10.6
	Undissolved water D 3240	X1.10.7
Miscellaneous	Additives	X1.11.1
	Sample containers	X1.11.2

INSPECTION DATA ON AVIATION TURBINE FUELS

(See the back of the form itself or Specification D 1655 Appendix A2 for instructions on use of form)

REPORT DATE _____ QUANTITY U.S. GALLONS: _____

CONTRACT No. _____ SAMPLING LOCATION: _____

ORDER No. _____ DESTINATION: _____

DATE SAMPLED _____ PRODUCT NAME: _____

SAMPLE No. _____ COMPLIES WITH SPECIFICATIONS: _____ REMARKS: _____

BATCH No. _____

TANK No. _____

GRADE _____

Method	APPEARANCE	Results
10 D 156	Color (Saybolt)	
20 —	Visual (B=Bright & C=Clear)	
	COMPOSITION	
100 D 974/3242	Acidity, Total (mg KOH/g)	
110 D 1319	Aromatics (vol %)	
120 D 1319	Olefins (vol %)	
130 D 3227 1	Sulfur, Mercaptan (wt %)	
140 D 484	Doctor Test (P=Pos, N=Neg)	
150 D 1266/1552/2622	Sulfur, Total (wt %)	
	VOLATILITY	
200 D 86	Distillation Ind. BP (F)	
205 D 86	" 10% Rec (F)	
210 D 86	" 20% Rec (F)	
215 D 86	" 50% Rec (F)	
220 D 86	" 90% Rec (F)	
225 D 86	" 95% Rec (F)	
230 D 86	" Final BP (F)	
235 D 86	Residue (%)	
240 D 86	Loss (%)	
245 D 86	Recovery at 400 F (%)	
250 FTMS 1151	Explosiveness (vol %)	
260 D 56/3828	Flash Point, Tag Closed (F)	
261 D 93	Flash Point, Pensky Martin (F)	
270 D 1298	Gravity, API (60 F)	
280 D 1298	Gravity, Specific (60/60 F)	
290 D 323	Vapor Pressure (lb Reid)	
	FLUIDITY	
300 D 2386	Freezing Point (F)	
310 D 445	Viscosity at -30 F (cSt)	
	COMBUSTION	
400 D 1405	Aniline Gravity Product	
410 D 1405	Net Heat of Comb. (Btu/lb)	
420 D 1740	Luminometer No.	
430 D 1322	Smoke Point	
440 D 1840	Naphthalenes (vol %)	
450 D 1655	Smoke-Volatility Index	

Method	CORROSION	Results
500 D 130	Copper Strip (2h at 212F)	
510 IP 227	Silver Strip	
	STABILITY	
600 D 1660	Coker Δ P (in. Hg)	
610 D 1660	Coker Tube Color Code	
611 D 3241	JFTOT at 260C ΔP (mm Hg)	
612 D 3241	JFTOT at 260C Tube Color Code	
613 D 3241	JFTOT at 260C TDR Spun Rating	
614 D 3241	JFTOT at 245C Δ P (mm Hg)	
615 D 3241	JFTOT at 245C Tube Color Code	
616 D 3241	JFTOT at 245C TDR Spun Rating	
	CONTAMINANTS	
700 IP 225	Copper Content (μg/kg)	
710 D 381	Existent Gum (mg/100 ml)	
720 D 2276	Particulates (mg/liter)	
721 Mil-T-5624J APP A	Filtration time, min	
722 "	vacuum, mm Hg	
723 "	volume fuel filtered, ml	
740 D 1094	Water Reaction Interface Rating	
741 D 1094	" Separation Rating	
750 D 2550	WSIM	
751 D 3602	MSS	
752 D 3948	MSEP	
	ADDITIVES	**Brand**
800 Anti-icing (vol %)		
810 Antioxidant (lb/M Bbl)		
820 Corrosion Inhib (lb/M Bbl)		
830 Metal Deactivator (lb/M Bbl)		
840 Antistatic, mg/liter		
	OTHER TESTS	
900 D 2624/3114	Conductivity (pS/m)	
901 D 2624/3114	" Temperature (F)	

APPROVED BY _____ _____

Company Representative — Authorized Government Representative

American Society for Testing and Materials

ASTM D1655

PCN 12-416552-00

FIG. X1.1 Standard Form for Reporting Inspection Data on Aviation Turbine Fuels

Designation: D 975 – 81[ε1]

An American National Standard

Standard Specification VI.4

Standard Specification for DIESEL FUEL OILS[1]

This standard is issued under the fixed designation D 975; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

[ε1] NOTE—New Section 2 was editorially added and subsequent sections renumbered; also Figs. X2.1 through X2.12 were editorially changed in May 1982.

1. Scope

1.1 This specification covers three grades of diesel fuel oils suitable for various types of diesel engines.

1.2 This specification, unless otherwise provided by agreement between the purchaser and the supplier, prescribes the required properties of diesel fuels at the time and place of delivery.

NOTE 1—Nothing in this specification shall preclude observance of federal, state, or local regulations which may be more restrictive.

1.3 The values stated in SI units are to be regarded as the standard. The values stated in inch-pound units are for information only.

2. Applicable Documents

2.1 *ASTM Standards:*

D 56 Test for Flash Point by Tag Closed Tester[2]

D 86 Method for Distillation of Petroleum Products[2]

D 93 Tests for Flash Point by Pensky-Martens Closed Tester[4]

D 129 Test for Sulfur in Petroleum Products (General Bomb Method)[5]

D 130 Detection of Copper Corrosion from Petroleum Products by the Copper Strip Tarnish Test[6]

D 270 Sampling Petroleum and Petroleum Products[6]

D 445 Test for Kinematic Viscosity of Transparent and Opaque Liquids (and the Calculation of Dynamic Viscosity)[5]

D 482 Test for Ash from Petroleum Products[6]

D 524 Test for Ramsbottom Carbon Residue of Petroleum Products[6]

D 613 Test for Ignition Quality of Diesel Fuels by the Cetane Method[7]

D 976 Calculated Cetane Index of Distillate Fuels[6]

D 1500 Test for ASTM Color of Petroleum Products (ASTM Color Scale)[5]

D 1796 Test for Water and Sediment in Crude Oils and Fuel Oils by Centrifuge[8]

D 2161 Conversion of Kinematic Viscosity to Saybolt Universal Viscosity or to Saybolt Furol Viscosity[9]

D 2274 Test for Oxidation Stability of Distillate Fuel Oil (Accelerated Method)[8]

D 2276 Test for Particulate Contaminant in Aviation Turbine Fuels[8]

D 2500 Test for Cloud Point of Petroleum Oils[8]

D 2880 Specification for Gas Turbine Fuel Oils[8]

D 3117 Test for Wax Appearance Point of Distillate Fuels[10]

3. Requirements

3.1 The grades of diesel fuel oils herein spec-

[1] This specification is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants.

Current edition approved Aug. 28, 1981. Published October 1981. Originally published as D 975 – 48 T. Last previous edition D 975 – 78.

[2] *1983 Annual Book of ASTM Standards*, Vols 05.01 and 06.03.

[4] *Annual Book of ASTM Standards*, Vols 05.01, 06.01, and 06.03 and *1982 Annual Book of ASTM Standards*, Part 22.

[5] *Annual Book of ASTM Standards*, Vol 05.01 and *1982 Annual Book of ASTM Standards*, Part 40.

[6] *Annual Book of ASTM Standards*, Vol 05.01.

[7] *Annual Book of ASTM Standards*, Vol 05.04.

[8] *Annual Book of ASTM Standards*, Vol 05.02.

[9] *Annual Book of ASTM Standards*, Vol 05.02 and *1982 Annual Book of ASTM Standards*, Part 40.

[10] *Annual Book of ASTM Standards*, Vol 05.03.

ified shall be hydrocarbon oils conforming to the detailed requirements shown in Table 1.

4. Test Methods

4.1 The requirements enumerated in this specification shall be determined in accordance with the following methods:

4.1.1 *Flash Point*—Method D 93, except where other methods are prescribed by law. For Grades No. 1-D and No. 2-D, Method D 56, may be used as an alternate with the same limits, provided the flash point is below 79°C (175°F) and the viscosity is below 5.5 cSt (or mm^2/s)[11] at 40°C (104°F). This method will give slightly lower values. In cases of dispute, Method D 93 shall be used as the referee method.

4.1.2 *Cloud Point*—Method D 2500. Method D 3117 may also be used since the two are closely related. In case of dispute Method D 2500 shall be the referee method.

4.1.3 *Water and Sediment*—Method D 1796.

4.1.4 *Carbon Residue*—Method D 524.

4.1.5 *Ash*—Method D 482.

4.1.6 *Distillation of No. 1-D and No. 2-D Fuel Oils*—Method D 86.

4.1.7 *Viscosity*—Method D 445 or by conversion in accordance with Method D 2161.

4.1.8 *Sulfur*—Method D 129.

4.1.9 *Corrosion*—Method D 130, 3 h test at 50°C.

4.1.10 *Cetane Number*—Method D 613.

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[11] One centistokes (1cSt) equals one millimetre squared per second (1 mm^2/s); therefore, the two units are interchangeable.

TABLE 1 Detailed Requirements for Diesel Fuel Oils[A,H]

Grade of Diesel Fuel Oil		Flash Point, °C (°F)	Cloud Point °C	Water and Sediment, vol %	Carbon Residue on, 10 % Residuum, %	Ash, weight %	Distillation Temperatures, °C (°F)		Viscosity				Sulfur,[D] weight %	Copper Strip Corrosion	Cetane Number[E]
							90 % Point		Kinematic, cSt[G] at 40°C		Saybolt, SUS at 100°F				
		Min	Max	Max	Max	Max	Min	Max	Min	Max	Min	Max	Max	Max	Min
No. 1-D	A volatile distillate fuel oil for engines in service requiring frequent speed and load changes	38 (100)	[B]	0.05	0.15	0.01	...	288 (550)	1.3	2.4	...	34.4	0.50	No. 3	40[F]
No. 2-D	A distillate fuel oil of lower volatility for engines in industrial and heavy mobile service.	52 (125)	[B]	0.05	0.35	0.01	282[C] (540)	338 (640)	1.9	4.1	32.6	40.1	0.50	No. 3	40[F]
No. 4-D	A fuel oil for low and medium speed engines.	55 (130)	[B]	0.50	...	0.10	...	...	5.5	24.0	45.0	125.0	2.0	...	30[F]

[A] To meet special operating conditions, modifications of individual limiting requirements may be agreed upon between purchaser, seller, and manufacturer.

[B] It is unrealistic to specify low-temperature properties that will ensure satisfactory operation on a broad basis. Satisfactory operation should be achieved in most cases if the cloud point (or wax appearance point) is specified at 6°C above the tenth percentile minimum ambient temperature for the area in which the fuel will be used. The tenth percentile minimum ambient temperatures for the United States are shown in Appendix X2. This guidance is of a general nature; some equipment designs, use flow improver additives, fuel properties, or operations, or a combination thereof, may allow higher or require lower cloud point fuels. Appropriate low temperature operability properties should be agreed upon between the fuel supplier and purchaser for the intended use and expected ambient temperatures.

[C] When cloud point less than −12°C (10°F) is specified, the minimum viscosity shall be 1.7 cSt (or mm^2/s) and the 90 % point shall be waived.

[D] In countries outside the United States, other sulfur limits may apply.

[E] Where cetane number by Method D613 is not available, Method D976 may be used as an approximation. Where there is disagreement, Method D613 shall be the referee method.

[F] Low-atmospheric temperatures as well as engine operation at high altitudes may require use of fuels with higher cetane ratings.

[G] 1 cSt = 1 mm^2/s.

[H] The values stated in SI units are to be regarded as the standard. The values in inch-pound units are for information only.